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Hydrogeologic and Geochemical Studies of Selected Natural Radioisotopes and Barium in Groundwater in Illinois

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HYDROGEOLOGIC AND GEOCHEMICAL STUDIES
OF SELECTED NATURAL RADIOISOTOPES
AND BARIUM IN GROUNDWATER IN ILLINOIS

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ABSTRACT

Dissolved concentrations of the natural radioisotopes ^{222}Rn , ^{226}Ra , ^{228}Ra , ^{230}Th , ^{232}Th , ^{234}U and ^{238}U and the element Ba^{2+} were investigated in a study of high concentrations of ^{226}Ra , ^{228}Ra , and Ba^{2+} in groundwater from the Cambrian and Ordovician bedrock of northern Illinois. The high radium and barium concentrations are naturally present in the major aquifers—the sandstone bedrock; therefore, remedial well construction measures will not lower the concentrations. The combined concentrations of ^{226}Ra and ^{228}Ra range from 2.3 to 50.2 pCi/L; the majority of analyses exceed the limit in the drinking water regulations of 5.0 pCi/L. The $^{226}\text{Ra}/^{228}\text{Ra}$ activity ratio ranges from 0.2 to 41.0; a ^{226}Ra analysis has no validity for predicting the ^{228}Ra concentration. Important controls on dissolved ^{226}Ra concentrations are secondary U on the sandstone matrix and the ionic strength of groundwater. The distribution of accessory minerals that contain ^{232}Th is believed to be an important control on dissolved ^{228}Ra concentrations. Locally the dissolved ^{226}Ra and ^{228}Ra concentrations are affected by dissolution-precipitation of secondary barite. Dissolved concentrations of ^{222}Rn and U are less than proposed drinking water regulations. The extreme enrichment in ^{234}U that occurs widespread in groundwater from the Cambrian and Ordovician bedrock is unique and problematic. The enrichment may reflect recharge of uranium to the bedrock by glacial processes. Dissolved Ba^{2+} concentrations range from <0.01 to 22.4 mg/L. The high Ba^{2+} concentrations occur in groundwater that is depleted in dissolved SO_4^{2-} by anaerobic microbial reactions. A map presents the distribution of Ba^{2+} in groundwater from the Cambrian and Ordovician bedrock in northeastern Illinois.

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HYDROGEOLOGIC AND GEOCHEMICAL STUDIES OF SELECTED NATURAL RADIOISOTOPES AND BARIUM IN GROUNDWATER IN ILLINOIS

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The high disequilibrium between uranium-234 and uranium-238 in groundwater from the Cambrian and Ordovician bedrock in some localities of Illinois was first noted by J. K. Osmond, Geology Department, Florida State University, Tallahassee, Florida.

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INTRODUCTION

This report presents findings from a study of the geochemical mechanisms responsible for the occurrence of two isotopes of the radioactive element radium (radium-226 in the uranium-238 decay series and radium-228 in the thorium-232 decay series) and the element barium in groundwater of Illinois at concentrations that exceed the limits imposed in the National Interim Primary Drinking Water Regulations (U.S. Environmental Protection Agency, 1975). The barium is not radioactive. The high radium and barium concentrations are largely restricted to groundwater from bedrock of the Cambrian and Ordovician Systems in northern Illinois. Radium and barium are both alkaline-earth cations with similar chemical properties. The occurrence of these elements in groundwater is discussed in separate sections of this report.

The present research has generated several reports. A report by Gilkeson et al. (1978) presented analyses of rock samples for barium and radioactive elements and discussed general mechanisms important to the occurrence of barium and radium in groundwater. Perry, Grundl, and Gilkeson (1982) reported on the distribution of stable isotopes of oxygen, hydrogen, and sulfate in groundwater from the Cambrian and Ordovician bedrock. Gilkeson, Perry, and Cartwright (1981) discussed evidence that the anomalous depletion of sulfate in groundwater with high barium concentrations was due to bacterially mediated chemical reactions. Gilkeson and Cowart (1982) described the extreme enrichment in uranium-234 in groundwater from the Cambrian and Ordovician bedrock.

This report presents analyses for chemical constituents, including barium and radium, for raw groundwater samples from wells in communities of northern Illinois. It is important to note that the concentrations of radium and barium in the analyses may not reflect the concentrations of these constituents in the finished water supplied to the consumer. The efficient removal of radium and barium by two conventional water treatment processes (ion exchange softening and lime softening) was determined in a study by Bennett, Bell, and Markwood (1976). Several communities use these treatment processes.

Many communities in northern Illinois produce groundwater from several wells that are finished in different aquifers. In general, groundwater produced from aquifers other than the Cambrian and Ordovician bedrock has very low concentrations of radium and barium. The blending of groundwater from these other aquifers with groundwater from the Cambrian and Ordovician bedrock may result in a finished groundwater that is in compliance with the drinking water regulations. Surface water supplies also have very low concentrations of radium and barium. Chicago and many other communities are supplied water from Lake Michigan. The City of Elgin in northeastern Illinois has recently completed construction of a facility to treat water from the Fox River. Several other communities in northern Illinois use rivers or reservoirs for water supplies.

HYDROGEOLOGIC SETTING AND MAJOR IONS IN GROUNDWATER

Public groundwater supplies are produced from the Cambrian and Ordovician bedrock in a fairly extensive area of northern Illinois (fig. 1). South of the study area water quality in the Cambrian and Ordovician is undesirable because of the high concentrations of dissolved minerals in the groundwater. The radioactive element section of this report is concerned with the entire area shown in figure 1. The barium section of the report is primarily concerned with the Cambrian and Ordovician bedrock in restricted localities in the northeastern and northwestern regions of figure 1.

A generalized column of rock-stratigraphic units in northern Illinois is shown in figure 2. The Cambrian and Ordovician bedrock is composed of thick sections of sandstone and dolomite interbedded with shale. In downward order, the stratigraphic units are the Maquoketa Shale Group, Galena and Platteville Dolomite Groups, Glenwood-St. Peter Sandstone and Prairie du Chien Group of Ordovician age, the Eminence Formation, Potosi Dolomite, Franconia Formation, Ironton-Galesville Sandstone, Eau Claire Formation, and Mt. Simon Sandstone. Shale in the upper part of the Eau Claire Formation is a significant aquitard hydraulically separating the Ironton-Galesville Sandstone from the Elmhurst Sandstone Member (basal Eau Claire) and the Mt. Simon Sandstone.

On a regional scale the significant aquifers are the sandstones, including the St. Peter, the Ironton-Galesville, the Elmhurst Member in the basal Eau Claire Formation, and the Mt. Simon Sandstones. The Ironton-Galesville Sandstone is the most productive aquifer over a major part of the study area. Production of groundwater from wells is often increased through the detonation of explosives in the Ironton-Galesville section of the open borehole.

The yield of groundwater from the dolomite bedrock units is variable, depending upon the number and areal interconnections of joints, fractures, and crevices. The contribution of groundwater from the shale bedrock to the open borehole is generally small.

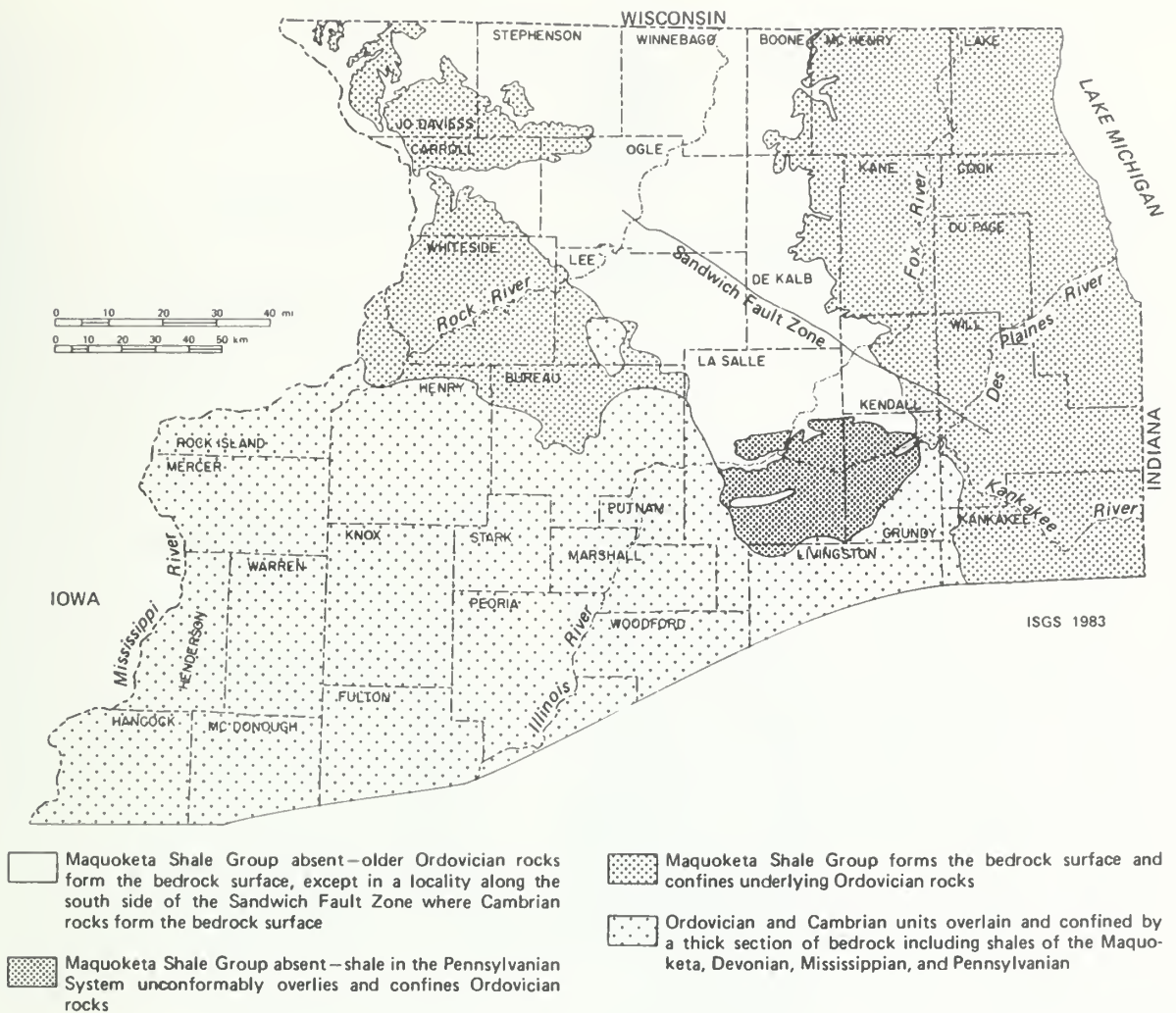


FIGURE 1. Geologic map of the area of northern Illinois where groundwater supplies are produced from the Cambrian and Ordovician bedrock. Sources of information are Willman et al. (1967) and Willman et al. (1975).




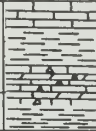

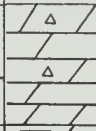



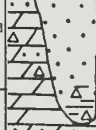





SYSTEM	SERIES	GROUP OR FORMATION	LOG	THICKNESS (m)	DESCRIPTION
Quaternary	Pleistocene			0-180	Unconsolidated glacial deposits - pebbly clay (till), silt, and gravel; loess (windblown silt), and alluvial silt, sand, and gravels.
Tertiary and Cretaceous				0-30	Sand and silt.
Pennsylvanian				0-150	Mainly shals with thin sandstones, limestone and coal.
Mississippian	Valmeysran	St. Louis Salem Warsaw Keokuk- Burlington		0-180	Limestones; cherty limestone; green, brown and black shale; silty dolomite.
	Kindsrhookian				
Devonian				0-120	Shals, calcareous; limestone attrata, thin.
Silurian	Niagaran			0-140	Dolomite, silty at base, locally cherty.
	Alexandrien	Kankakee Edgwood			
Ordovician	Cincinnatian	Maquoketa		0-75	Shals, gray or brown; locally dolomite and/or limestone, argillaceous.
	Champlainian	Galena		0-140	Dolomits and/or limestones, cherty; Dolomits, shals partings, speckled; Dolomite and/or limestones, cherty, sandy at base.
		Plattsville			
		Glenwood			
		St. Peter		0-200	Sandstone, fine- and coarse-grained; little dolomits; shale at top. Sandstone, fine- to medium-grained; locally cherty red shale at base.
	Canadian	Prairie du Chien Group Shakopee New Richmond Oneota		30-400	Dolomits, sandy, cherty (oolitic), sandstone. Sandstone, interbedded with dolomits. Dolomits, white to pink, coarse-grained, cherty (oolitic), sandy at base.
Cambrian	Croixan	Eminence and Potosi			
		Franconia		20-80	Dolomits, white, fine-grained, nodular quartz, sandy at base.
		Ironton			Dolomits, sandstone, and shals, glauconitic, green to red, micaceous.
		Galeaville			Sandstone, fine- to medium-grained, well sorted, upper part dolomitic.
		Eau Claire Proviso Lombard Elmhurst		75-140	Shale and siltstone; dolomite, glauconitic; sandstone, dolomitic, glauconitic.
		Mt. Simon		150-790	Sandstone, coarse-grained, white, red in lower half; lenses of shale and siltstone, red, micaceous.
Precambrian					

FIGURE 2. Generalized column of rock-stratigraphic units in northern Illinois.

The oxidation-reduction potential (Eh) of groundwater in the Cambrian and Ordovician bedrock was investigated through measurements on groundwater in an airtight flow chamber that contained two platinum electrodes coupled to a calomel reference electrode. The measurement technique is discussed by Back and Barnes (1965). In the present study, the potentials were monitored using two separate platinum electrodes as a check for spurious values. The pH of groundwater was also measured in the airtight flow chamber.

Whitfield (1974) performed thermodynamic analyses to quantitatively define the chemical reactions that constrain the measurement of Eh with the platinum electrode. In well-oxygenated aqueous systems the platinum metal is sensitive to formation of platinum oxide coatings. In anaerobic aqueous systems that contain sulfide ion, the metal is sensitive to formation of sulfide coatings. The calculations by Whitfield (1974) indicate that for the pH range of groundwater in the Cambrian and Ordovician bedrock the platinum electrode would respond as an inert metal over the approximate range in potential of +300 to 0 millivolts.

Figure 3 presents the relation of Eh values measured with the platinum electrode to the total sulfide concentration in groundwater at wells that produce from the Cambrian and Ordovician bedrock. The range in Eh is from +400 to -180 millivolts. The values greater than +300 millivolts were measured in primary recharge zones where the Cambrian and Ordovician bedrock is unconfined. The high values may be due to the presence of dissolved oxygen in the groundwater.

The total concentration of dissolved sulfide species in groundwater was measured at wells with the titrimetric (iodine) method (Standard Methods, 1971). The method has a lower limit of detection of 0.1 mg/L. At many wells, sulfide was detected by odor at concentrations too small to be measured. Figure 3 shows that the potentials measured with the platinum electrodes were sensitive to the concentration of dissolved sulfide present in the groundwater. Sulfide was not present in groundwater samples with Eh values greater than 100 millivolts and was rarely present at concentrations greater than 0.1 mg/L in groundwater

with Eh greater than +50 millivolts. Sulfide concentrations greater than 1.0 mg/L poised the Eh of groundwater in a range from -50 to -100 millivolts; these Eh values may not accurately represent the oxidation-reduction potential of the groundwater. The groundwater pumped from the majority of wells is a mixture of groundwater produced from several stratigraphic units open to the well bore. The sulfide concentration and the oxidation-reduction potential in groundwater produced from each of the discrete units may be very different. A general finding for the eastern part of the study area is that where sulfide is present in groundwater, the high concentrations are in the Galena and Platteville Groups and the Glenwood-St. Peter Sandstone. The lowest Eh value of -180 millivolts was measured at a well where the concentration of sulfide in groundwater was less than 0.1 mg/L; a concentration too low to poise the potentials measured with the platinum electrodes. The relation between the platinum electrode values of Eh and the dissolved sulfide concentrations in the groundwater is consistent with the relation observed by Berner (1963) for natural and artificial sulfide-bearing sediments.

Figure 1 shows that the Maquoketa Shale Group is absent over much of the north-central and northwestern part of the study area, and that older rocks form the bedrock surface. In the northwestern region the Maquoketa Shale Group is present on some uplands and confines underlying rocks. In some localities where the Maquoketa is absent, fine-grained glacial drift and/or dense unfractured dolomite of the Galena and Platteville Groups serve as confining units.

The terrane setting is an important control on the configuration of groundwater flow systems in the north-central and northwestern regions. Uplands are zones of recharge to the Cambrian and Ordovician bedrock, and river valleys are zones of discharge. Water level measurements have defined a north-south groundwater divide through the eastern part of the region (fig. 4). A portion of the groundwater recharge that occurs eastward of the divide enters a regional groundwater flow system in the northeastern part of the study area.

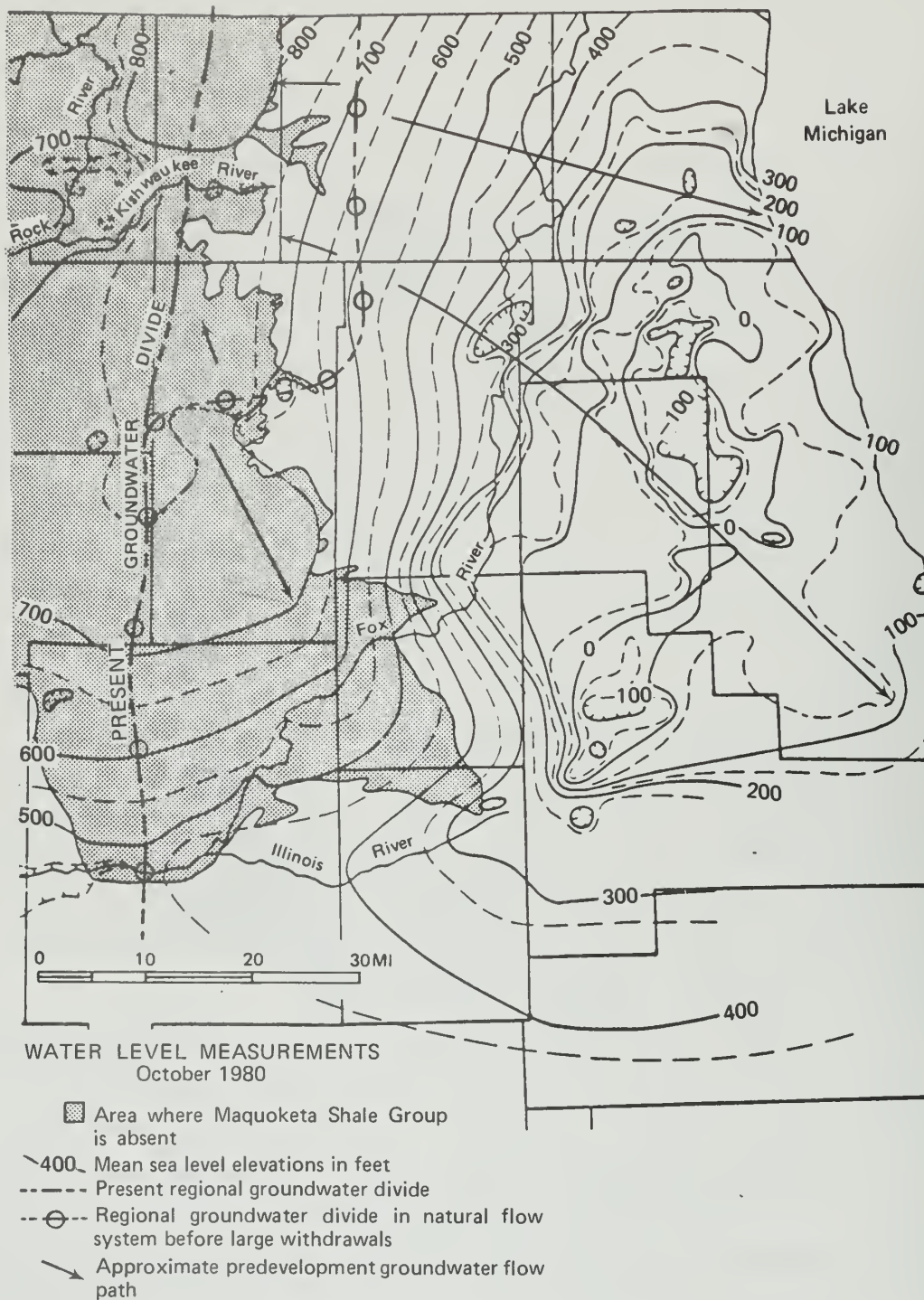


FIGURE 4. The potentiometric surface in a region of northeastern Illinois for wells that produce groundwater from the Ironton-Galesville Sandstone and overlying Cambrian and Ordovician rocks. Water level measurements were taken in October 1980. The figure also illustrates the effect of the large groundwater withdrawals on groundwater flow in the regional system (modified from Sasman et al., 1982).

In the north-central and northwestern regions groundwater is produced from rock-stratigraphic units from the Galena through the Mt. Simon Sandstone. The concentration of total dissolved minerals in the groundwater ranges from approximately 250 mg/L to 600 mg/L. Groundwater with concentrations of total dissolved minerals of less than 400 mg/L is produced from many wells across this part of the study area that are drilled deep into the Mt. Simon. The pH of groundwater produced from wells ranges from 7.0 to 7.5. The major cations in the groundwater are calcium and magnesium and the major anion is bicarbonate. The concentration of sulfate is generally less than 30 mg/L. The Eh of groundwater measured with platinum electrodes ranged from +400 to +15 millivolts. The highest values were measured at wells located in primary recharge zones and may reflect the presence of dissolved oxygen in the groundwater. The lowest values were measured at wells where the aquifer units are confined. Hydrogen sulfide was often present in the confined groundwater, but generally at concentrations less than 0.1 mg/L.

In the northeastern part of the study area, the Cambrian and Ordovician bedrock is confined by the Maquoketa Shale Group. When the first wells were drilled in the 1860s, the artesian pressure in the Cambrian and Ordovician bedrock was sufficient to cause wells to flow in the Chicago-Joliet-Fox River valley area. As a result of large withdrawals of groundwater, the potentiometric surface over the period from 1864 to 1980 has declined more than 900 feet in localities in northern Cook and northeastern Du Page Counties (Visocky, 1982). By 1980 substantial dewatering of the upper stratigraphic units in the Ordovician bedrock had occurred in major pumping centers (table 1). Figure 4 shows the potentiometric surface in the fall of 1980 for wells in northeastern Illinois that produce groundwater from the Ironton-Galesville Sandstone and overlying stratigraphic units in the Cambrian and Ordovician System. The -100-foot contour outlines the major pumping centers. Groundwater flow is from all directions toward these centers. The shape of the potentiometric surface indicates that groundwater transmitted to these pumping centers is primarily from the west and north and to a lesser extent from the south and east.

TABLE 1

Stratigraphic Units of the Ordovician System
in Northeastern Illinois That Were Dewatered in 1980
(Modified from Visocky, 1982)

<u>Pumping Center</u>	
Aurora	More than 2/3 of the Galena and Platteville Groups
Elgin	More than 2/3 of the Galena and Platteville Groups
E. Du Page-W. Cook Co.	All of the Galena and Platteville Groups and less than 1/4 of the Glenwood-St. Peter Sandstone
Joliet	All of the Galena and Platteville Groups and nearly 1/4 of the Glenwood-St. Peter Sandstone
N. Cook Co.	All of the Galena and Platteville Groups and more than 1/3 of the Glenwood-St. Peter Sandstone

Most of the wells in the northeastern region have open boreholes in the stratigraphic interval from the Galena Group through the Ironton-Galesville Sandstone. Some wells are also open to the Eau Claire Formation and the Mt. Simon Sandstone. Care has to be taken in completing wells in the Mt. Simon because of the presence of highly mineralized groundwater at depths greater than several hundred feet into the sandstone. The large withdrawals of groundwater have resulted in the Ironton-Galesville Sandstone, the unit with the highest transmissivity, having a lower hydraulic head than the overlying and underlying bedrock. During periods when a well is not pumped, a cross-formational flow of groundwater occurs in the open borehole in response to differences in hydraulic head between the formations. The lower head in the Ironton-Galesville results in recharge of groundwater to this stratigraphic unit from overlying bedrock in the open borehole. If the well bore is also open to the underlying Eau Claire or to the Mt. Simon, then groundwater will flow up the open borehole from these stratigraphic units and out into the Ironton-Galesville during periods of nonpumpage.

The exact configuration of the potentiometric surface of the Cambrian and Ordovician before extensive groundwater withdrawal is unknown. Interpretation of data from early studies indicates that under

natural conditions the surface was relatively featureless and sloped gently to the southeast (Suter et al., 1959). Terrane features such as highlands on glacial moraines and major drainageways such as the Fox, Des Plaines, Kankakee, and Illinois Rivers must have had a significant effect on hydraulic gradients of the natural potentiometric surface.

The present location of the regional groundwater divide (fig. 4) along the western side of Boone and De Kalb Counties is a result of the change in hydraulic pressure caused by the large withdrawals of groundwater from the Cambrian and Ordovician bedrock. Estimated flow lines for the regional groundwater flow in bedrock of the Cambrian and Ordovician of northeastern Illinois before the large withdrawals of groundwater are shown on figure 4. The flow lines are based on an interpretation from the earliest water level measurements (Suter et al., 1959) and from consideration of regional terrane relations. The flow lines are intended only as an approximation of groundwater movement in the regional flow system and do not show the effects due to anisotropy or heterogeneity in the rock strata.

The axis of the regional groundwater divide in the natural flow system trended north to south through McHenry County and the northwestern part of Kane County. The north to south axis also extends north of McHenry County across Walworth County, Wisconsin. In Kane County the axis of the divide turned westward across De Kalb County. The high topographic elevations along the Marengo Moraine are an important control of the position of the regional groundwater divide in McHenry and Kane Counties in Illinois, and Walworth County in Wisconsin. The end moraine was constructed in Woodfordian time (late Wisconsinan) during the first major glacial event following the period of cool climatic conditions and weak soil development that occurred during the Farmdalian Substage (22,000 to 20,000 years before the present) (Kempton and Gross, 1971).

Pre-Woodfordian terrane relations (mapped by S. S. Wickham and W. H. Johnson, 1981) indicate that prior to construction of the Marengo Moraine the natural regional groundwater divide was located farther west approximately at the position of the present divide. During this

earlier time (before construction of the Marengo Moraine) primary recharge to the regional flow system of northeastern Illinois occurred over a large area of Boone and northern De Kalb Counties where the Maquoketa Group is absent. However, after construction of the Marengo Moraine recharge to the regional flow system no longer occurred in this area of Boone and De Kalb Counties and recharge was limited to the slow infiltration of groundwater through a thick sequence of fine-grained geologic materials including shale of the Maquoketa and glacial till.

In the northeastern region the concentration of total dissolved minerals in groundwater ranges from approximately 250 mg/L to 2050 mg/L. The lowest concentrations are present along the western part of the region; mineralization increases to the east and southeast along the direction of groundwater flow. The pH of groundwater produced from wells in the region varies from 7.0 to 7.5. Calcium, magnesium, and bicarbonate are the dominant ions in the dilute groundwaters. The anomalous depletion of sulfate ion in groundwater in the northwestern part of the region is discussed in the barium section of this report. Downgradient from the depleted zone, sulfate concentrations increase rapidly (fig. 11) and are present at concentrations greater than 800 mg/L in southeastern Cook County. The concentrations of sodium and chloride are also significant in the mineralized groundwater.

Hydrogen sulfide is commonly present in groundwater from wells within the zone of sulfate depletion and ranges in concentration from <0.1 mg/L to 6.0 mg/L. At these well sites the high sulfide concentrations are present in the groundwater from the Galena and Platteville Groups and the Glenwood-St. Peter Sandstone. Eh values for these wells range from +50 to -100 millivolts. Downgradient from the anaerobic environment there is a rapid increase in the Eh of groundwater, with values ranging from +150 to +300 millivolts occurring in Du Page, Cook, and Lake Counties.

Over a major part of the southeastern region of the study area (fig. 1, east and south of the Illinois River and south of the Kankakee River) the Cambrian and Ordovician bedrock is confined by the Pennsylvanian System and/or the Maquoketa Group. The Pennsylvanian is absent in the eastern part of the region.

The Maquoketa Group is absent because of erosion in the north-central part of the region over an area that includes the western part of Grundy County and all but the southwestern part of La Salle County. In most of the area where the Maquoketa is eroded, the Cambrian and Ordovician bedrock are confined by shales of the Pennsylvanian System. An exception is a restricted area in southern La Salle County (fig. 1) where the Pennsylvanian is eroded and the Galena and Platteville or the Glenwood-St. Peter form the bedrock surface beneath the glacial drift.

Groundwater in the Cambrian and Ordovician bedrock in the southeastern region is highly mineralized within a short distance of confinement. Only along the northern part of this region are wells constructed to produce groundwater from the Ironton-Galesville. No wells in the region produce groundwater from the Eau Claire or the Mt. Simon. In this region the concentration of total dissolved minerals in groundwater from the Cambrian and Ordovician bedrock ranges from approximately 300 mg/L to 1500 mg/L. The pH of groundwater produced from wells ranges from 7.1 to 7.6. Sodium and chloride are the major ions in the more mineralized groundwater. At some wells the chloride concentration exceeds 500 mg/L. Other ions that occur at appreciable concentrations in the groundwater are calcium, magnesium, sulfate, and bicarbonate. The groundwater at most wells contains hydrogen sulfide with the concentration of total dissolved sulfides ranging from <0.1 mg/L to 4.5 mg/L. Eh measurements with the platinum electrode method vary from +30 to -180 millivolts.

In the southwestern part of the study area (the region west of the Illinois River on fig. 1) the Cambrian and Ordovician bedrock is confined by a thick section of bedrock including shale of the Maquoketa, Mississippian, and Pennsylvanian. The Pennsylvanian forms the bedrock surface except where absent along the western margin. The Cambrian and Ordovician bedrock in the southwestern region is part of a large regional groundwater flow system that has zones of primary recharge in northwestern Iowa (Horick and Steinhilber, 1978).

Most wells in the southwestern region are constructed to produce groundwater from stratigraphic units from the Galena through the

Glenwood-St. Peter. Only in the larger communities are the wells constructed to also produce groundwater from the Iron-ton-Galesville. No wells in the region produce groundwater from the Eau Claire or the Mt. Simon.

Groundwater in the Cambrian and Ordovician bedrock in the southwestern region is highly mineralized. The concentration of total dissolved minerals in groundwater ranges from approximately 1,000 mg/L in the northern part of the area to concentrations greater than 3,000 mg/L at a few wells in the southern part. The pH of groundwater produced from wells ranges from 7.1 to 7.5. The major ions in the groundwater are calcium, magnesium, sodium, bicarbonate, sulfate, and chloride. At many wells the concentration of dissolved sulfate exceeds 1,000 mg/L. Groundwater from wells in the southern part of the area commonly has fluoride concentrations that exceed 2.0 mg/L, the limit set in the drinking water regulation (U.S. EPA, 1975).

Dissolved sulfide species are ubiquitous in groundwater from the Cambrian and Ordovician bedrock in the southwestern region; concentrations range from less than 0.1 to 0.9 mg/L. The groundwater has a low Eh (values for platinum electrode measurements range from -10 to -50 millivolts).

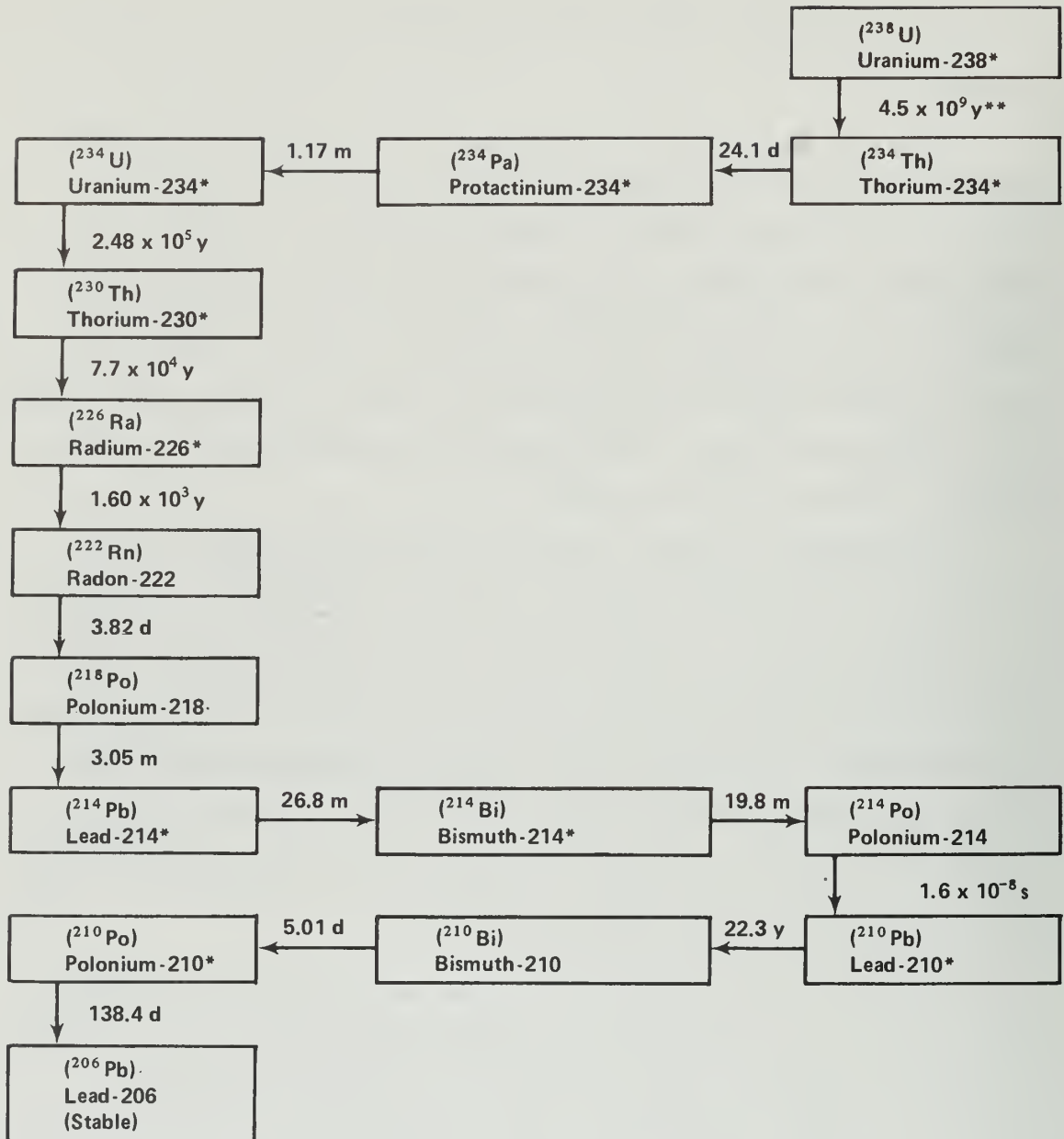
NATURAL RADIOISOTOPES IN GROUNDWATER

BACKGROUND

The study of geochemical mechanisms that control the occurrence of radium-226 and radium-228 in groundwater requires knowledge of the distribution of other radioactive elements in the decay series. This report presents information on the occurrence of the following isotopes in groundwater: uranium-238 (^{238}U), uranium-234 (^{234}U), thorium-230 (^{230}Th), radium-226 (^{226}Ra), and radon-222 (^{222}Rn) in the ^{238}U decay series and thorium-232 (^{232}Th), radium-228 (^{228}Ra), and radium-224 (^{224}Ra) in the ^{232}Th decay series. The information presented on the occurrence of ^{232}Th , ^{230}Th and ^{224}Ra is limited.

The naturally occurring long-lived radioactive elements ^{238}U (99.3 percent of the natural uranium) and ^{232}Th (effectively 100 percent of the natural thorium) are the parents of the radioactive decay series shown in figures 5 and 6. The nuclides in the two decay series, along with the long-lived radioactive element, ^{40}K (potassium-40), account for practically all of the natural environmental radiation of terrestrial origin. ^{235}U (uranium-235) is the long-lived parent nuclide of the actinium decay series. Because of the very small amount of ^{235}U relative to ^{238}U , the natural environmental concentration of radioisotopes in the actinium decay series is insignificant.

The rate of disintegration of a radioactive element is constant and is commonly expressed as the half-life, the period of time required for the disintegration of half the atoms in a sample of a specific radioactive element. As figures 5 and 6 illustrate, the half-lives for specific radioactive elements represent an extreme range of values. The long-lived parent nuclides of the two decay series were formed in a primary stellar nuclear synthesis process and were in existence at the time of formation of the earth; their abundances in the earth have been decreasing through geologic time because of their radioactivity. The daughter nuclides in the ^{238}U and ^{232}Th decay series are too short-lived to be remnants of the earth's formation. The nuclides are re-generated in nature by decay of the parent nuclides.



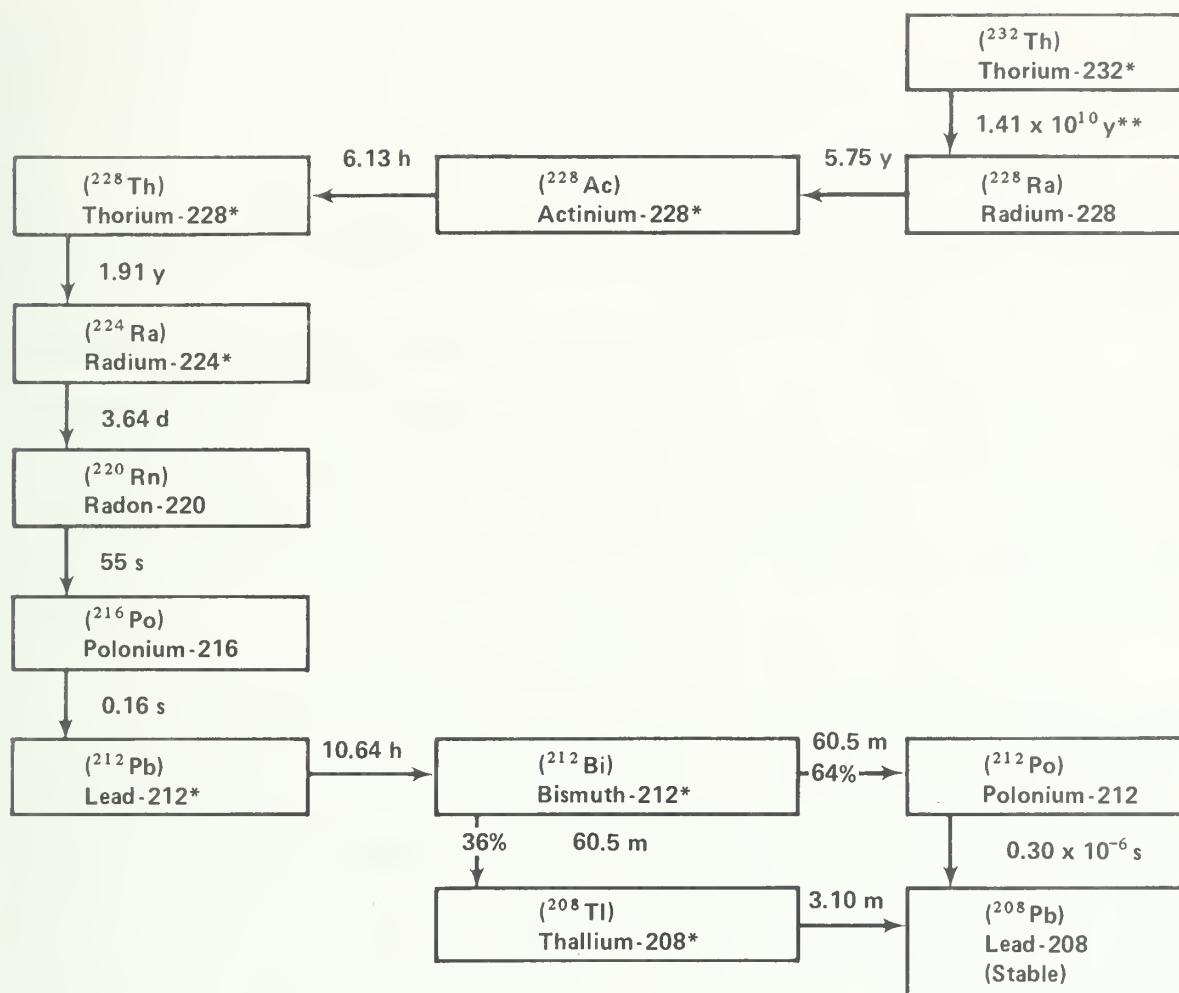
Note: Vertical direction represents alpha decay; horizontal direction represents beta decay.

* Also gamma emitters

** Times shown are half-lives: y = years; d = days; h = hours; m = minutes; s = seconds

ISGS 1983

FIGURE 5. The radioactive decay series of uranium-238.



Note: Vertical direction represents alpha decay; horizontal direction represents beta decay.

* Also gamma emitters

** Times shown are half-lives: y = years; d = days; h = hours; m = minutes; s = seconds

ISGS 1983

FIGURE 6. The radioactive decay series of thorium-232.

The radioactivity of an unstable isotope is by definition

$$A = N\lambda \quad (1)$$

where A is activity in disintegrations per unit time, N is the number of atoms in the system and λ is the decay constant—the fraction of atoms decaying per unit time. In a closed system in which radioactive elements are neither added or removed except by radioactive decay, a state of secular equilibrium will eventually be achieved between radioactive parents and daughters. At equilibrium the activities of parent and daughter nuclides are equal. Although the activities are the same at equilibrium, the mass concentrations of the parent-daughter nuclides are greatly different. For example, at secular equilibrium, the mass ratio of ^{234}U to ^{238}U is 0.000056.

In open systems, such as groundwater flow systems, secular equilibrium between parent and daughter nuclides is seldom found because of different mobilities due to the chemical properties of the radioactive elements. The disequilibrium that is measured between two radioactive elements of a decay series is commonly expressed as the ratio of their activities. At equilibrium the activity ratio equals 1.

The disintegration of a radioactive nuclide is accompanied by the release of energy in the form of alpha, beta, or gamma radiation. Alpha and beta are forms of particulate radiation; gamma radiation is composed of photons (extremely minute packets of radiant energy). An alpha particle is composed of the nucleus of a helium atom (the two orbiting electrons are missing) that is emitted from the nucleus of the decaying nuclide at a high velocity. Ultimately, all alpha particles emitted from radioactive elements find two electrons in the environment and become helium gas. A beta particle is an electron emitted at a high velocity from a decaying nuclide. The decay series in figures 5 and 6 present information on the type of radiation emitted by specific radioactive elements.

The curie, named in honor of Madame Marie Curie, is the unit used as the standard rate of disintegration. Originally, the curie was defined as the number of disintegrations occurring per second from one gram of pure ^{226}Ra . Because this number could change over time because of increased counting accuracy or improvements in purifying ^{226}Ra

samples, the decision was made to define the curie at a stable standard value that was close to, but not tied to, the decay rate for ^{226}Ra . The curie is now defined as that quantity of radionuclide that is disintegrating at a rate of 3.7×10^{10} disintegrations per second. Refined measurements have determined the activity of one gram of ^{226}Ra to be 3.61×10^{10} disintegrations per second (0.98 curies). The units used in this report to express the content of many of the radioactive elements in water are picocuries per liter (pCi/L). One picocurie is equal to 1×10^{-12} curies or 2.22 disintegrations per minute.

Radiation produces damaging effects in living tissue through a process called ionization. Ionizing radiation introduces energies to living tissue that are huge in comparison with ordinary chemical reactions. The radiation has the potential to remove electrons from atoms that comprise living tissue. These electrons have a great capacity to break chemical bonds as they travel through living tissue causing the release of other electrons. The atoms of living tissue that lose electrons become ions with such a high state of energy that they can produce chemical reactions that would never have been possible without the ionizing radiation.

All three radiations (alpha, beta, and gamma) have the potential to cause ionizations. High-energy gamma radiation may pass through living tissue with few ionizations. The efficiency of alpha and beta particles for inducing ionizations is related to the charge on the particle and the velocity of the particle. The higher the charge and the more slowly a particle is travelling, the greater is the chance for ionization. Therefore, the highly charged, slow moving alpha particles have the greatest potential to cause ionizations.

RADIUM ISOTOPES IN GROUNDWATER

Four natural isotopes of radium may occur in groundwater: ^{226}Ra (1600-year half-life) in the ^{238}U decay series, ^{228}Ra (5.75-year half-life) and ^{224}Ra (3.64-day half-life) in the ^{232}Th decay series, and ^{223}Ra (11.4-day half-life) in the ^{235}U decay series. The immediate parent nuclides of all four natural radium isotopes are isotopes of the element thorium.

The concentrations of ^{223}Ra present in the natural environment are insignificant because of the very slight concentrations of its long-lived parent, ^{235}U . No analyses for ^{223}Ra were performed in this research.

No drinking water regulation relative to ^{224}Ra has been promulgated. There is little public health concern for this isotope because of its short half-life of 3.64 days. The source for ^{224}Ra in groundwater is ^{228}Th that is present on the aquifer matrix; the concentration of ^{228}Th in groundwater is insignificant. Groundwater pumped from a well is removed from the parent thorium nuclide, and depending upon the residence time of the water in the distribution system before consumption, a significant reduction of the ^{224}Ra concentration may occur because of the short half-life. Also, because of its short half-life, ^{224}Ra will not accumulate in the human skeleton, but a portion of the ^{224}Ra that is ingested will be present on the surface of bones, delivering alpha radiation to sensitive tissue. The longer lived radium isotopes (^{226}Ra and ^{228}Ra) have residence in the interior of bones where tissue is less sensitive to ionizing radiation.

The short half-life of ^{224}Ra presents difficulty to the design of an effective monitoring program for a large number of water supply wells. Analyses for this isotope in groundwater of Illinois are restricted to a limited number of measurements reported by Stehney (1955). In groundwater samples collected in 1951 and 1952 at eight wells in northern Illinois that produce groundwater from the Cambrian and Ordovician bedrock, the concentration of ^{224}Ra ranged from 4.9-7.3 pCi/L. The values are similar in magnitude to the concentration of ^{228}Ra measured in groundwater at well sites in the same localities. The relation between ^{224}Ra and ^{228}Ra concentrations requires further investigation. If a close relation is found, then ^{228}Ra measurements may be an indicator of ^{224}Ra concentrations. If the values for ^{224}Ra and ^{228}Ra are found to be similar, then the activity concentration of ^{224}Ra in potable groundwater from the Cambrian and Ordovician bedrock will be expected to range from approximately 1.0 to 20 pCi/L. Activity concentrations of this magnitude will not be of concern for public health.

Of the radioactive elements present in groundwater, ^{226}Ra and ^{228}Ra are of most concern with respect to public health. Radium is often described as a "bone seeker." Because the human body metabolizes radium and calcium similarly, the continuous ingestion of trace concentrations of ^{226}Ra and ^{228}Ra over a long period of time will result in an accumulation of radium in the skeleton. After deposition in bone tissue, radium leaves the body very slowly. The daughter nuclides of ^{226}Ra and ^{228}Ra have short half-lives. Therefore, the disintegration of either radium nuclide initiates a series of disintegration events over a short interval of time. As shown in figures 5 and 6, many of the short-lived daughter nuclides emit alpha particles upon disintegration. The high specific activity (alpha-particle emission per unit weight) of radium is an important concern of the nuclides to public health.

The incidence of bone-cancers related to ingestion of large quantities of ^{226}Ra and ^{228}Ra is well known (Argonne National Laboratory, 1981). However, the relation between chronic ingestion of low concentrations of radium and health risk is not well established. Nevertheless, the U.S. Environmental Protection Agency (1975) promulgated the following National Interim Primary Drinking Water Regulations concerning radioactivity in drinking water:

1. The average annual gross alpha contaminant level shall not exceed 15 pCi/L.
2. The combined ^{226}Ra and/or ^{228}Ra contaminant level shall not exceed 5 pCi/L.

The interim regulations allow substitution of a gross alpha contaminant level of 5 pCi/L or less for the radium analyses and do not require a ^{228}Ra analysis unless the ^{226}Ra activity concentration exceeds 3 pCi/L. A weakness of these provisions is that in the absence of alpha emitters, the contaminant level of ^{228}Ra present is not determined. U.S. Environmental Protection Agency recognized this deficiency and therefore provided for augmented monitoring by individual states. The National Interim Primary Drinking Water Regulations recommend that in localities where ^{228}Ra may be present in drinking water, the states require ^{226}Ra and ^{228}Ra analyses when the gross alpha particle activity exceeds 2 pCi/L. Compliance with this recommendation would require

^{226}Ra and ^{228}Ra analyses at nearly all well sites in Illinois where groundwater is produced from the Cambrian and Ordovician bedrock.

The presence of high activity concentrations of ^{226}Ra in groundwater from bedrock of the Cambrian and Ordovician Systems was reported in papers by Stehney (1955), Lucas and Ilcewicz (1958), Emrich and Lucas (1963), and Holtzman (1964). Analyses for both ^{226}Ra and ^{228}Ra in groundwater from bedrock of the Cambrian and Ordovician were presented in reports by Krause (1959, 1960). The analytical data from these historical studies have been incorporated into this report. In addition, this report incorporates previously unpublished analyses on ^{228}Ra in groundwater provided by Dr. Henry Lucas of the Argonne National Laboratory.

In the present research, groundwater samples were collected from carefully selected wells distributed across the study area. Unfiltered and filtered (0.22 micron pore size membrane) samples were collected at the well head, and preserved with nitric acid or EDTA. The radon emanation method of Lucas (1977) was used for analyses of ^{226}Ra . The analytical procedure for ^{228}Ra is described in Krieger and Whittaker (1980).

The Relation Between Gross Alpha Radiation and Radium-226 in Groundwater

The Illinois Environmental Protection Agency performed analyses for gross alpha and gross beta radiation on untreated groundwater samples from municipal wells in Illinois; most of the analyses were performed from 1971 to 1976. Over the period of study the analyses were repeated several times for most wells. The gross radiation analysis was a useful screening method to identify regions where high concentrations of radioactive elements may occur in groundwater. Potable groundwater with a very low gross alpha concentration will also have a very low ^{226}Ra concentration. For wells with low gross alpha radiation concentrations (<3 pCi/L), all repeated analyses over the 6-year study measured low concentrations. However, at wells where gross alpha concentrations of 5 pCi/L or greater were measured, concentrations found by repeated analyses were variable. The most variation occurred in groundwater samples with the highest concentrations. A general trend indicated in the gross alpha analyses for many wells was an increase in concentration

in the later analyses. Therefore, a concern developed that over time the groundwater was increasing in radioactivity. An objective of the present research was to identify the mechanisms responsible for the variation over time in the gross alpha concentration.

Table 2 presents gross alpha radiation analyses and ^{226}Ra analyses for selected wells where historical analyses on ^{226}Ra were available. The gross alpha radiation analyses were performed by the Illinois Environmental Protection Agency. All of the ^{226}Ra analyses were performed at the Argonne National Laboratory. A large variation in gross alpha radiation values was found for most of the wells, although for most wells the variation in ^{226}Ra concentrations is small or insignificant. On the basis of a few analyses performed by the Illinois Environmental Protection Agency, Gilkeson et al. (1978) reported in a preliminary study that filtration (0.22 micron pore size membrane) had a significant effect on reducing the gross alpha radiation in groundwater having high values. Two examples of this apparent effect are shown in table 2 for the duplicate samples collected at municipal well Lynwood-2 (7/27/77) and at municipal well Lstant-4 (7/25/77). The lower alpha radiation values in each set were for filtered groundwater. Actually, filtration does not have significant effects on the concentration of gross alpha radiation: the variation in gross alpha radiation concentrations at the well sites in table 2 was primarily due either to the method of analysis or to analytical error. The method for analysis of gross alpha radiation and the implication of the analysis to the concentration of ^{226}Ra in groundwater are discussed in the following paragraphs.

When radioactive equilibrium with respect to ^{226}Ra is attained in the sample prepared for gross alpha particle analysis four alpha particles are emitted for every ^{226}Ra atom that decays. This is illustrated in the ^{238}U decay series presented in figure 5, starting with ^{226}Ra . The vertical downward sequence indicates that a nuclide disintegrates with emission of an alpha particle while the horizontal sequence indicates that a nuclide disintegrates with release of beta radiation. As illustrated in the figure, the ^{226}Ra decays to ^{222}Rn (radon-222), an inert gas with a 3.82-day half-life, which in turn decays to ^{218}Po (polonium-218), and then to ^{214}Pb (lead-214). At that point two beta

TABLE 2

Gross Alpha Radiation and Radium-226 in Groundwater for
Repeated Measurements at Selected Wells

County Owner, Well No.	Collection Date (pCi/L)	Gross Alpha Radiation ^a (pCi/L)	²²⁶ Ra
Cook Lynwood-2	12-05-72	52 ± 15	-
	03-27-75 ^c	149 ± 27	14.7
	04-02-75 ^c	156 ± 26	14.4
	04-10-75 ^c	58 ± 16	14.9
	10-08-75	78 ± 19	-
	07-27-77 ^d	140 ± 20	-
	07-27-77 ^d	74 ± 17	-
	08-04-79	-	15.6
Kane Elgin-6	03-21-74	13 ± 4	-
	03-07-75 ^c	55 ± 7	13.3
	12-05-79	-	13.6
	06-03-80	-	11.5
La Salle Lostant-4	1958 ^e	-	9.9
	08-05-72	24 ± 7	-
	05-05-75	34 ± 10	-
	07-25-77	56 ± 12	-
	07-25-77	12 ± 6	-
	12-04-79	-	10.6
Livingston Odell-3	1958 ^e	-	11.2
	10-05-72	33 ± 10	-
	06-02-75	24 ± 8	-
	08-21-80	-	10.7
Peoria Elmwood-3	1958 ^e	-	8.2
	02-27-73	32 ± 10	-
	10-08-75	39 ± 11	-
	03-28-76	43 ± 12	-
	11-05-80	-	7.9

- a. Gross alpha radiation analyses performed by the Illinois Environmental Protection Agency. The coefficient of variation is shown for each analytical value.
- b. ²²⁶Ra analyses performed by Argonne National Laboratory, coefficient of variation—± 3%.
- c. Analytical data from Bennett, Bell, and Markwood (1976).
- d. Analytical data from Gilkeson et al. (1978).
- e. Analytical data from Krause (1960).

decays form ^{214}Po (polonium-214), which then decays by alpha emission to ^{210}Pb (lead-210). For purposes of this analysis the series ends with ^{210}Pb because the nuclide has a long half-life (22.3 years) and thus decays very slowly.

In the analysis of gross alpha radiation, a measured quantity of water is evaporated to dryness, forming a thin residue of the dissolved constituents on a counting planchet. The evaporation is done at high heat to drive off ^{222}Rn gas present in the water. If all of the ^{222}Rn were driven off and a period of 4 hours elapsed between preparation of the planchet and counting of alpha activity, then none of the short-lived daughter products ^{218}Po , ^{214}Pb , ^{214}Bi and ^{214}Po would be present in the residue, since the longest half-life in the series is only 26.8 minutes. Thus, if the sample is counted 3 to 4 hours after preparation, only ^{226}Ra will be present at a significant concentration for the series ^{226}Ra to ^{210}Pb , and only one alpha particle is emitted for each ^{226}Ra atom decaying. The ^{222}Rn grows into the residue with a 3.82-day half-life; therefore, after about 4 days the ^{222}Rn would build up to one-half its maximum activity by the equation

$$A_{\text{Rn}} = A_{\text{Ra}} (1 - e^{-\lambda t}) \quad (2)$$

where A_{Rn} is the activity of ^{222}Rn , A_{Ra} is activity of the ^{226}Ra , e is the base of the natural logarithms with a value of 2.7183, λ is the radioactive constant of the isotope ^{222}Rn (for ^{222}Rn $\lambda = 0.693/3.82 = 0.1814 \text{ day}^{-1}$), and t is the time since the evaporation.

When the decay products of ^{222}Rn reach equilibrium with ^{222}Rn three alpha particles will be emitted for each atom of ^{222}Rn that decays; one from the ^{222}Rn and two from its daughters, ^{218}Po and ^{214}Po . Consequently, if we assume that all of the ^{222}Rn is retained in the residual film of the evaporated sample (actually, some of the ^{222}Rn will escape from the sample) and that the sample has one disintegration per minute of ^{226}Ra , then one alpha particle per minute will be emitted immediately after preparation. After 4 days about 3 alpha particles will be emitted per minute, one from the ^{226}Ra and two from the ^{222}Rn series; after 40 days (10 half-lives of the ^{222}Rn when the value of $e^{-\lambda t}$ in equation (2) becomes insignificant), the ^{222}Rn will be in radioactive equilibrium

with the ^{226}Ra and there will be 4 alpha particles emitted for each ^{226}Ra nuclide that decays. Additionally, a portion of the alpha particle activity may not be detected because the particles are absorbed by the matrix of the residue.

Table 3 presents repeated analysis for gross alpha particle activity for eight groundwater samples collected from wells that produce groundwater from stratigraphic units in the Cambrian and Ordovician Systems. Analyses were performed at Argonne National Laboratory with the interim radiochemical procedure recommended by the U.S. Environmental Protection Agency (Krieger, 1976). Unfiltered and filtered samples of groundwater were collected at each well. Table 3 also presents analyses for ^{226}Ra , ^{238}U , and ^{234}U in the groundwater samples.

All of the gross alpha radiation analyses show increase in alpha activity over time due to the grow-in of ^{222}Rn and the ^{222}Rn daughters in the residue on the counting planchets. For most of the samples the later gross alpha radiation analyses approached values that were between 3 and 4 times greater than the ^{226}Ra concentrations. Filtration did not have significant effects on either the ^{226}Ra concentrations or the gross alpha radiation concentrations; the differences noted on most samples are within the limits of the analytical method. However, the ^{226}Ra concentrations were slightly lower in filtered samples from municipal wells Orland Park-6, Homewood-12, and Lockport-4. The combined activity concentrations of ^{234}U and ^{238}U in the groundwater samples ranged from 0.02 to 2.8 pCi/L. ^{238}U and ^{234}U disintegrate through emission of alpha particles. Therefore, the gross alpha radiation concentrations presented in table 3 include a contribution from ^{234}U and ^{238}U that is equivalent to the concentrations of these nuclides reported in the table.

In the procedure recommended by the U.S. Environmental Protection Agency for analyses of gross alpha radiation in drinking water (Krieger, 1976) there are no specifications concerning the storage time of the planchet between preparation and counting. The procedure does not account for the grow-in of the short-lived daughter nuclides of ^{226}Ra into the residue on the counting planchet. It is obvious from the above discussion that a large range in the measured concentration of gross alpha radiation may occur in planchets with appreciable concentrations

TABLE 3

Uranium-234 + Uranium-238, Radium-226 and Gross Alpha Radiation
in Groundwater from Selected Wells^a

County	²³⁴ U + ²³⁸ U Well No. (pCi/L)	²²⁶ Ra ^b		Gross Alpha Radiation ^c			
		Unfil- tered (pCi/L)	Fil- tered ^d (pCi/L)	Planchet residence time (days)	Unfil- tered (pCi/L)	Planchet residence time (days)	Fil- tered (pCi/L)
Cook, Or- land Park-6	2.8	8.1	6.8	4	13.3	4	7.3
				12	11.1	12	7.9
				20	11.7	20	8.6
Cook, Home- wood-12	2.2	3.4	2.3	0	10.2	4	6.7
				6	12.1	12	11.3
				14	15.6	20	8.5
Cook, Lyn- wood-2	2.7	15.6	15.6	2	37.1	0	30.5
				14	48.4	7	49.7
				22	48.6	14	52.9
Fulton, Ta- ble Grove-1	0.4	15.0	15.2	0	21.9	0	29.3
				12	59.1	12	57.6
				14	55.4	14	64.5
Kane, Elgin-6	0.02	12.4	13.0	1	27.8	2	36.3
				13	30.8	14	39.7
				21	32.7	22	44.2
Kendall, Yorkville-4	0.6	7.9	8.1	2	16.6	0	17.6
				14	17.8	7	18.6
				22	18.3	18	21.7
						21	20.6
McDonough, Macomb-2	0.34	18.7	20.6	4	68.8	2	35.5
				12	77.4	14	68.9
				20	80.0	22	83.5
Will, Lock- port-4	2.7	10.7	9.4	4	20.9	1	15.4
				12	22.8	13	24.1
				20	23.7	15	24.3

- Radium-226 and gross alpha radiation analyses were performed on unfiltered and filtered samples. The data illustrate the variation in gross alpha radiation concentration that occurs as a function of counting planchet residence time.
- ²²⁶Ra analyses performed by Argonne National Laboratory; coefficient of variation—± 3%.
- Gross alpha radiation analyses performed at Argonne National Laboratory with analytical procedure given in Krieger (1976); coefficient of variation—± 30%.
- Samples were filtered at the well (0.22 micron pore size membrane) before the addition of preservatives.

of ^{226}Ra that are counted on a random time basis after preparation.

A significant part of the variation in the Illinois Environmental Protection Agency data set of gross alpha radiation analysis of water samples from specific wells over the period of 1971 to 1976 may be due to differences in storage time between preparation and counting of the planchets. However, in some of the analyses, the concentration of gross alpha radiation is significantly greater than the equilibrium value four times greater than the ^{226}Ra concentration. For example, three analyses for municipal well no. 2 at Lynwood (table 2) show a range of 140 to 156 pCi/L. These high values are difficult to explain and may represent laboratory error.

Gross alpha radiation analysis is obviously a valuable tool for rapidly screening the radioactivity of a water sample. Samples with low concentrations of gross alpha radiation will also have low concentrations of ^{226}Ra and other nuclides such as ^{234}U , that emit alpha radiation. However, for water samples that contain high concentrations of gross alpha radiation, no accurate finding can be made concerning the concentration of ^{226}Ra present. Because of the inaccuracy of the analytical method of performing the gross alpha radiation measurements, the existing data base of the Illinois Environmental Protection Agency cannot be used to investigate changes in radioactivity of the groundwater that may have occurred over the 6-year period during which the analyses were performed.

Regional Concentrations of Radium-226 and Radium-228 in Groundwater

In the analyses presented in this report on samples of potable groundwater from the Cambrian and Ordovician bedrock, the concentration of ^{226}Ra ranges from 0.1 pCi/L to a maximum value of 36.9 pCi/L, and the concentration of ^{228}Ra ranges from 0.5 pCi/L to a maximum value of 32.7 pCi/L. Figure 7 presents the relation of ^{226}Ra and ^{228}Ra concentrations in groundwater from 90 wells that produce groundwater from the Cambrian and Ordovician bedrock at wide scattered locations throughout the study area. For these wells the combined concentrations of the two nuclides range from 2.3 to 50.2 pCi/L. Only 4 of the combined analyses were in compliance with the maximum limit of the drinking

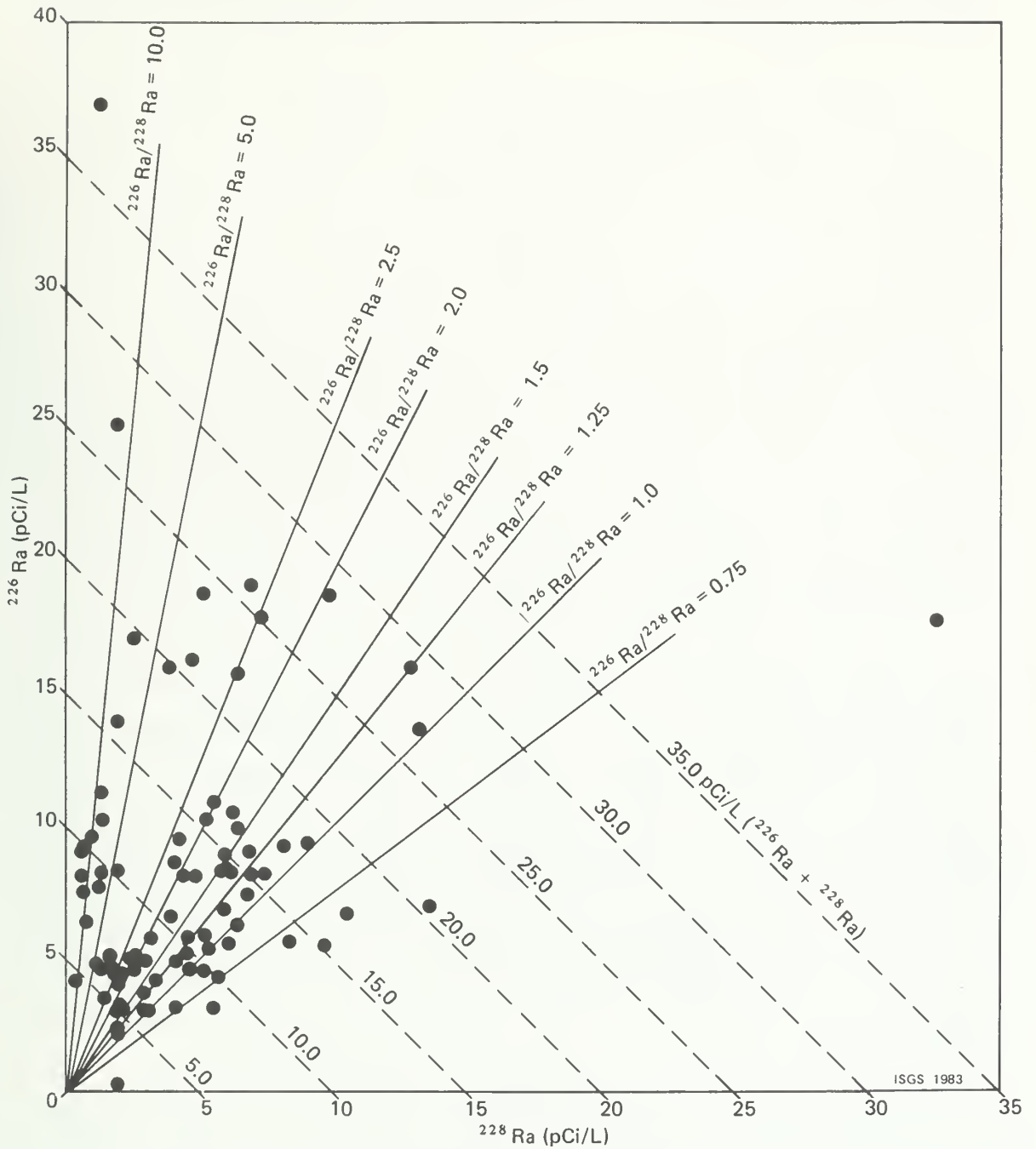


FIGURE 7. The low correlation coefficient between the concentration of radium-226 and radium-228 in groundwater from the Cambrian and Ordovician bedrock. For a least square line fit to the analyses, the correlation coefficient, r , = 0.275. Isolines show the combined concentration of the two nuclides and the $^{226}\text{Ra}/^{228}\text{Ra}$ activity ratio.

water regulations of 5.0 pCi/L for the combined concentration of ^{226}Ra and ^{228}Ra . The combined concentrations were 10.0 pCi/L or greater in 55 of the analyses.

The ratio of $^{226}\text{Ra}/^{228}\text{Ra}$ for the 90 combined analyses ranges from 0.2 to 41.0. The large range in values indicates that the ^{228}Ra concentration in groundwater cannot be predicted from a ^{226}Ra analysis. A least square line fit to the analyses determined a low correlation coefficient, r , of 0.275. In the analyses presented in this report, concentrations of ^{226}Ra of 5.0 pCi/L or lower were usually accompanied by concentrations of ^{228}Ra of 5.0 pCi/L or lower. However, analyses of groundwater from the Cambrian and Ordovician bedrock in Illinois, Iowa, Missouri, and Wisconsin by Lucas (1982) determined that high ^{228}Ra concentrations were occasionally present in groundwater with low ^{226}Ra concentrations. Analyses of groundwater samples in South Carolina by Michel and Moore (1980) and in Finland by Asikainen (1981) also found a low correlation between the concentrations of ^{226}Ra and ^{228}Ra .

Data available from analyses on ^{226}Ra and ^{228}Ra are too limited to be used to determine accurately the regional occurrence of the nuclides in potable groundwater from the Cambrian and Ordovician bedrock. However, some general trends in concentrations are apparent. Combined concentrations of ^{226}Ra and ^{228}Ra in groundwater from the Cambrian and Ordovician bedrock exceeding the maximum contaminant level of 5.0 pCi/L are widespread in Illinois. The lowest combined concentrations for the two nuclides occur in groundwater samples from well sites in the north-central and northwestern regions of the study area in zones of primary recharge where the Maquoketa Group is absent and groundwater has had a short residence time in the Cambrian and Ordovician bedrock.

The lowest ^{226}Ra concentrations in groundwater from the Cambrian and Ordovician bedrock (values of less than 2.0 pCi/L) are in zones of primary recharge in the north-central and northwestern regions of the study area where the Maquoketa Shale Group is absent. Downgradient of the primary recharge zones, the ^{226}Ra concentration in groundwater increases; however, for wells in the north-central and northwestern regions where the Maquoketa Shale Group is absent, the values seldom exceed 5.0 pCi/L with most values less than 4.0 pCi/L. Higher ^{226}Ra

concentrations occur in groundwater where the Cambrian and Ordovician bedrock are confined with the highest concentrations occurring in the mineralized groundwater zones.

In the southwestern, northwestern and north-central regions of the study area the ^{228}Ra concentrations in groundwater seldom exceed 3.0 pCi/L; the majority of the concentrations are less than 2.0 pCi/L. The highest concentrations of ^{228}Ra occur in groundwater from wells located in the eastern part of the study area. Areas where the ^{228}Ra concentrations commonly range from 5.0 to 8.0 pCi/L are along the Fox River valley in Kane County, the southern part of Cook County, Will County, Grundy County, the southern part of La Salle County, and the eastern part of Marshall County. At a few wells in Kane, Cook, and Will Counties the ^{228}Ra concentrations range from 10 to 19 pCi/L.

Comparison of the values determined in previous radium analyses of groundwater with the values determined in the present research indicates that no significant variation has occurred over time in the ^{226}Ra or ^{228}Ra concentrations in groundwater from the Cambrian and Ordovician bedrock. The analyses indicate that the radium concentration in native groundwater produced from a discrete stratigraphic unit at a specific well has remained essentially constant, but that at a specific well site the discrete stratigraphic units open to the well bore may each produce groundwater with markedly different radium concentrations. The analyses also established that in groundwater from the Cambrian and Ordovician bedrock the high radium concentrations occur in groundwater from the significant water producing strata—the sandstones.

Analytical data for the eastern part of the study area indicate that the highest ^{226}Ra and ^{228}Ra concentrations in potable groundwater are from the regionally most productive stratigraphic unit, the Ironton-Galesville Sandstone. Specific examples are presented in the following discussion of municipal wells at Elgin in northeastern Kane County, Orland Park in southern Cook County, Coal City and Morris in Grundy County, and Peru in La Salle County.

Municipal wells at Elgin are constructed with open boreholes to receive groundwater from a large section of bedrock. All of the wells are open to stratigraphic units from the Galena and Platteville Dolomite Groups downward through the Ironton-Galesville Sandstone. In addition, several wells at Elgin are also open to the Eau Claire Formation and the upper section of the Mt. Simon Sandstone. The wells at Elgin that produce groundwater with the highest dissolved radium concentrations are those that were developed with explosives to increase production of groundwater from the Ironton-Galesville. Examples are Elgin-6, with ^{226}Ra concentrations ranging from 11.5 to 13.6 pCi/L and a ^{228}Ra concentration of 13.4 pCi/L, and Elgin 5A, with ^{226}Ra concentrations ranging from 7.1 to 8.8 pCi/L. Lower radium concentrations occur in groundwater from municipal wells at Elgin that were not developed with explosives and therefore produce a smaller component of groundwater from the Ironton-Galesville. Examples are Elgin-4A, with a ^{226}Ra concentration of 4.6 pCi/L and a ^{228}Ra concentration of 4.6 pCi/L and Elgin-5, with ^{226}Ra concentrations ranging from 4.3 to 6.1 pCi/L and a ^{228}Ra concentration of 4.2 pCi/L. Note that groundwater from Elgin-5 and Elgin-6 has significantly different ^{226}Ra concentrations. The wells are located 198 meters (650 ft) apart and have open boreholes over the same stratigraphic interval. The significant difference between the two wells is that explosives were used in Elgin-6 to increase the production of groundwater from the Ironton-Galesville. Elgin municipal wells no. 5 and 6 are in a well field that is located along the Fox River on the north side of Elgin. Three other wells located in this well field are constructed with the borehole open to stratigraphic units from the Galena and Platteville through the upper section of the Mt. Simon. The ^{226}Ra concentrations in groundwater from two of these wells has been slightly less than 5.0 pCi/L for samples collected on two occasions. For these two wells explosives were not used to develop production of groundwater from the Ironton-Galesville Sandstone. The Ironton-Galesville section in the other municipal well that is open to the Mt. Simon (Elgin municipal well no. 1) was developed with explosives. The ^{226}Ra concentration in three groundwater samples collected from this well have ranged from 5.2 to 8.5 pCi/L. One analysis for ^{228}Ra determined a concentration of 4.6 pCi/L. During rehabilitation

of this well in 1960 it was discovered that the borehole below the Ironton-Galesville was obstructed, reducing the quantity of groundwater from the lower stratigraphic units. The highest ^{226}Ra concentration was present in a groundwater sample collected before the rehabilitation, when because of the obstruction the well produced a greater component of groundwater from the Ironton-Galesville. After rehabilitation the ^{226}Ra concentration in groundwater produced from the well decreased, with the lowest concentration, 5.2 pCi/L, being measured for the most recent sample collected. The Elgin analyses indicate that potable groundwater from the deeper stratigraphic units has lower concentrations of ^{226}Ra and ^{228}Ra than groundwater from the Ironton-Galesville.

Radium analyses were performed on groundwater samples from four municipal wells located at Orland Park in the southern part of Cook County. ^{226}Ra concentrations of 15.7 pCi/L and 17.8 pCi/L were measured in groundwater samples from two wells that were constructed to produce groundwater only from the Ironton-Galesville (^{228}Ra concentrations in the two wells were 6.5 and 7.4 pCi/L, respectively). Significantly lower concentrations of 8.1 pCi/L for ^{226}Ra and 4.9 pCi/L for ^{228}Ra were measured in a groundwater sample collected from a well that is open to stratigraphic units from the Galena through the Ironton-Galesville. The low radium concentrations in the groundwater sample are believed to be related to an anomalous change in the chemical composition of groundwater produced from this well. The available chemical analyses indicate that during the two year period after the well was put into service there was a gradual decrease in the concentration of calcium (from 69 to 29 mg/L), magnesium (from 23 to 13 mg/L), and sulfate (from 228 to 162 mg/L) in groundwater produced from the well. Over this period the concentration of total dissolved minerals has decreased from 847 to 720 mg/L. The mechanism responsible for the change in the chemical composition and the possible significance of this change to the concentration of radium in the groundwater is not understood at the present time. The municipal well (Orland Park no. 10) is a main supply well for the community and is pumped on a regular basis. If the change in chemical composition of the pumped groundwater were due to precipitation reactions occurring because of the mixing of incompatible groundwaters in the open borehole, then it is possible that the yield

of the well may decrease in the future because of a decrease in transmissivity. The downhole geophysical and sampling methods discussed in the case history for Elgin well no. 3A in the barium section of this report would have application in investigating the mechanism responsible for the anomalous chemical composition of groundwater produced by this well.

The Village of Coal City (situated in east-central Grundy County) has three wells that produce groundwater from the Cambrian and Ordovician bedrock. The borehole of municipal well no. 5 at Coal City is open to stratigraphic units from the Prairie du Chien Group through the Ironton-Galesville. A groundwater sample collected from this well has a ^{226}Ra concentration of 18.6 pCi/L and a ^{228}Ra concentration of 9.9 pCi/L. The two other public supply wells at Coal City do not produce groundwater from the Ironton-Galesville and have much lower radium concentrations. Well no. 4 at Coal City has an open borehole to stratigraphic units from the Galena and Platteville through the St. Peter. Groundwater collected from this well had a ^{226}Ra concentration of 9.2 pCi/L and a ^{228}Ra concentration of 8.2 pCi/L. The borehole of well no. 3 at Coal City is open to the Galena and Platteville. However, fractures and crevices in the dolomite may have open connections to the underlying Glenwood-St. Peter and therefore a large component of the groundwater produced from the well may be from the sandstone. A groundwater sample collected from this well had a ^{226}Ra concentration of 8.9 pCi/L and a ^{228}Ra concentration of 6.0 pCi/L. Although the highest concentrations are present in groundwater from the Ironton-Galesville the combined concentrations of the two radium isotopes in groundwater from the three wells ranges from 14.9 to 28.5 pCi/L.

Radium analyses on groundwater samples are available for three municipal wells at Morris. The village is located along the Illinois River in northeastern Grundy County. Morris well no. 4 has an open borehole to stratigraphic units from the Prairie du Chien Group through the Ironton-Galesville. ^{226}Ra concentrations in groundwater samples collected from this well in 1957 and 1980 are 8.2 and 8.4 pCi/L, respectively. Morris well no. 5 is constructed with an open borehole to stratigraphic units from the Galena and Platteville through the

Iron-ton-Galesville, and explosives were used to increase production from the Iron-ton-Galesville. A groundwater sample collected from this well in 1980 had a ^{226}Ra concentration of 8.2 pCi/L. The lowest radium concentrations are 3.2 pCi/L for ^{226}Ra and 5.8 pCi/L for ^{228}Ra in a groundwater sample collected in 1957 from Morris well no. 3 when the borehole was open to stratigraphic units from the Galena through the Glenwood-St. Peter. In 1975 this well was deepened and constructed with an open borehole to stratigraphic units from the Galena through the Iron-ton-Galesville. A ^{226}Ra concentration of 4.4 pCi/L was measured in a groundwater sample collected in 1980 after the well was deepened. Although this concentration is greater than the value measured before the well was deepened, it is significantly lower than the ^{226}Ra concentrations measured in municipal wells no. 4 and 5. A possible reason for the lower concentration in well no. 3 is that explosives were not used to increase production of groundwater from the Iron-ton-Galesville.

^{226}Ra analyses on groundwater samples are available for four municipal wells at Peru. The city is located along the Illinois River in western La Salle County. The highest concentration, 6.5 pCi/L, was measured in a groundwater sample from Peru well no. 8. This well has an open borehole to stratigraphic units from the Galena through the Iron-ton-Galesville. Explosives were used to increase the production of groundwater from the Iron-ton-Galesville. The other three Peru municipal wells (no. 5, 6, and 7) are located in close proximity to one another. All three wells are constructed with open boreholes to stratigraphic units from the Galena through the Iron-ton-Galesville. The significant difference in the construction of the three wells is that explosives were used in well no. 7 to increase production of groundwater from the Iron-ton-Galesville. Groundwater produced from well no. 7 has a higher ^{226}Ra concentration, 6.1 pCi/L, than groundwater from the other two wells. The concentration of radium-226 in Peru wells no. 5 and 6 ranges from 3.1 to 4.8 pCi/L. The only ^{228}Ra analysis available for Peru wells is a concentration of 2.6 pCi/L measured in a groundwater sample from well no. 6.

The public supply wells that produce groundwater with the highest ^{226}Ra concentrations are located in the southwestern region of the study

area. These wells produce highly mineralized groundwater from the stratigraphic interval Galena through Glenwood-St. Peter. ^{226}Ra concentrations are commonly greater than 10.0 pCi/L, with values greater than 20.0 pCi/L at a few well sites. It is notable that the ^{228}Ra concentration in groundwater at well sites in the southwestern region are commonly less than 2.0 pCi/L. The precise concentration of ^{226}Ra in groundwater from the Ironton-Galesville in the southwestern region is not known.

The highest concentration of ^{226}Ra measured in the present research was 40.2 pCi/L for a sample of brine collected with a downhole sampler from the lower section of the Mt. Simon at a stratigraphic test boring located in the northeastern corner of Lake County in northeastern Illinois.

Mechanisms That Control the Concentrations of Radium Isotopes in Groundwater

Because of the differences in radium concentrations that may exist in groundwater from discrete stratigraphic units at a specific well, alterations in the well construction or a change in the rate and duration of pumpage may result in a change in the concentration of radium in groundwater produced from the well. The fact that the highest radium concentrations are found in groundwater from the Ironton-Galesville in the northeastern region indicates that an increase in the radium concentration in groundwater may occur in the future at wells located within the major pumping centers (fig. 4; table 1). As dewatering of the Galena and Platteville and the Glenwood-St. Peter proceeds in the pumping centers, the component of groundwater produced from the Ironton-Galesville will be increased.

In addition to the differences in radium concentrations in groundwater from discrete stratigraphic units open to a well bore, there may also be significant differences in the chemical composition of major ions in the groundwater. The mixing of dissimilar groundwaters in the well bore may result in secondary precipitation of mineral species. Some of these chemical reactions result in an efficient coprecipitation of radium. Study at several wells in northeastern Illinois has established that precipitation of secondary barite in the well bore may

result from the mixing of incompatible groundwaters from discrete stratigraphic units. At these wells the precipitation of secondary barite is often affected by the rate and duration of pumpage. The coprecipitation of radium in the barite may result in a significant decrease in the concentration of radium in groundwater produced from the well. The efficient coprecipitation of radium with barium to form the sulfate is a well-known phenomenon (Gordon and Rowley, 1957). The radium concentration is higher during periods when secondary barite precipitation is not occurring. Part of the increase in the radium concentration during these periods may be due to the mobilization of radium from the secondary barite.

Several geochemical and radiochemical mechanisms may be significant controls on the concentration of a radium isotope in groundwater. An inherent difficulty in determining the significant mechanisms are the ultratrace concentrations of radium isotopes present in solution. For the analyses presented in this report on potable groundwater, the activity concentration of ^{226}Ra ranges from approximately 0.1 to 36.9 pCi/L and is equivalent to a radium mass concentration that ranges from 1.0×10^{-10} to 3.8×10^{-8} mg/L. For comparison, the maximum value of 32.7 pCi/L measured for ^{228}Ra in potable groundwater is equivalent to a radium mass concentration of only 1.2×10^{-10} mg/L. The combined mass concentrations of ^{228}Ra , ^{224}Ra , and ^{223}Ra that occur in groundwater are insignificant relative to the mass concentration of ^{226}Ra .

The study of the distribution of radioactive elements in groundwater flow systems must include consideration of the residence time of groundwater in relation to the half-life of the radioactive elements. Laboratory experiments by Starik (1963) have demonstrated that nuclides of the short-lived isotopes, ^{224}Ra and ^{223}Ra , are released from the solid matrix of crushed minerals to solution at a rate that is dependent on their radioactive half-life. The accumulation of the nuclide into solution is described by equation (2) written in the following form:

$$A_t = A_e (1 - e^{-\lambda t}) \quad (3)$$

where A_t is the concentration in disintegration units at time t , and A_e is the equilibrium concentration in disintegration units.

Equation (3) illustrates that if disintegration of the thorium parent on the matrix is of primary significance to supplying the radium nuclide to solution (Starik, 1963; Cherdyntsev, 1971), the concentration of radium nuclides in groundwater may increase with an increase in the residence time of the groundwater in the aquifer. Therefore, the presence of low dissolved ^{226}Ra concentrations in groundwater in primary recharge zones may be due to the short residence time of groundwater. However, the concentrations of ^{226}Ra and ^{228}Ra present in groundwater with long residence time in confined regions of groundwater flow systems would reflect the abundance of their parent sources in the aquifer matrix (Cherdyntsev, 1971).

The $^{226}\text{Ra}/^{228}\text{Ra}$ activity ratio for 90 groundwater samples from the Cambrian and Ordovician bedrock in the study area ranges from 0.2 to 13.1, excluding an anomalously high value of 41.0 for a public supply well at Toulon in Stark County. (The radium concentrations in groundwater from this well are discussed later in this report.) As shown on figure 7 most analyses are enriched in ^{226}Ra and have activity ratios ranging between 1 and 5. Fifteen analyses show values greater than 5. The high ratios are evidence of an enrichment on the matrix of the ^{226}Ra parent nuclides (^{238}U and ^{234}U) relative to their normal abundance in rocks. The accumulation of ^{234}U and ^{238}U on the sandstone matrix is due to the transport of the nuclides in groundwater.

Study of the occurrence in groundwater of the nuclides in the ^{238}U decay series that precede ^{226}Ra and of the ^{222}Rn nuclide generated by disintegration of ^{226}Ra yields information on significant mechanisms that control the occurrence of ^{226}Ra in groundwater. In all groundwater samples analysed in this research the ^{222}Rn concentration was greater than the ^{226}Ra concentration by at least one order of magnitude. At wells where ^{226}Ra concentrations in groundwater were low, the ^{222}Rn concentrations were commonly 2 to 3 orders of magnitude greater than the ^{226}Ra concentrations. Some of the highest ^{222}Rn concentrations were measured in groundwater with the lowest ^{226}Ra concentrations. The short half-life of ^{222}Rn (3.82 days) precludes significant migration in groundwater from its site of origin. The short half-life also precludes a significant contribution of ^{222}Rn to solution by diffusion

from a site of generation within minerals (Tanner, 1964A). The ^{222}Rn concentrations in groundwater are evidence that ^{226}Ra is ubiquitous on the surfaces of the aquifer matrix; however, geochemical mechanisms strongly limit the concentration of ^{226}Ra present in groundwater.

In the present research, unfiltered and filtered groundwater samples were collected at numerous wells to determine the ^{226}Ra concentration on fine particulate matter that may be present in the groundwater. The analytical results for the majority of the filtered and unfiltered samples were identical within the limits of analytical accuracy. The ^{226}Ra was present in groundwater as dissolved species; very little of the ^{226}Ra was present adsorbed on particulate matter. The filtered and unfiltered concentrations for a limited number of samples are presented in table 3.

Equilibrium solubility with a mineral phase is not a controlling mechanism on the concentration of radium in groundwater from the Cambrian and Ordovician bedrock. Radium sulfate (RaSO_4) with a solubility product of $10^{-10.4}$ is the most insoluble of the alkaline earth sulfates and is also the most insoluble radium salt known (Kirby and Salutsky, 1964). However, the maximum concentrations of radium measured in groundwater from the Cambrian and Ordovician bedrock are many orders of magnitude less than allowed by the solubility of RaSO_4 .

Although radium does not form pure mineral species in natural systems, there is great potential for the element to precipitate from solution during the formation of other mineral species. For example, radium is very efficiently coprecipitated with barium in the formation of the mineral barite (BaSO_4) (Gordon and Rowley, 1957). Data gathered in the present study at several wells have determined that in groundwater that has a significant concentration of barium the precipitation-dissolution of barite may be an important control on the radium concentration.

Barite does not emanate ^{222}Rn generated by disintegration of coprecipitated ^{226}Ra (Hahn, 1936). Therefore, coprecipitation of ^{226}Ra in secondary barite is not a suitable mechanism to explain the high ^{222}Rn concentrations that are present in groundwater with very low ^{226}Ra concentrations in primary recharge zones in the north-central region of

the study area. Geochemical mechanisms that may be responsible for the low ^{226}Ra concentrations in groundwater in the recharge zone are coprecipitation of radium with calcium or magnesium to form carbonates or coprecipitation of radium with iron or magnesium to form hydrous oxides. Researchers who have studied groundwater in hydrogeological environments similar to primary recharge zones in north-central Illinois have attributed low ^{226}Ra and high ^{222}Rn concentrations to these coprecipitation mechanisms (Miholic, 1958; Tanner, 1964B).

The immediate parent of all ^{226}Ra is ^{230}Th present on the aquifer matrix; however, the ultimate source of all ^{226}Ra is ^{238}U , the long-lived parent isotope of the decay series. The precursor nuclides to ^{226}Ra , in order of occurrence, are ^{238}U , ^{234}Th , ^{234}Pa , ^{234}U , and ^{230}Th . Significant disequilibrium between the nuclides may occur in groundwater flow systems because of differences in the chemical and radiological properties of the nuclides. Analyses in this research have determined the widespread existence of extreme disequilibrium between ^{234}U and ^{238}U in groundwater from the Cambrian and Ordovician bedrock. The groundwaters are greatly enriched in ^{234}U . The enrichment is thought to reflect the widespread presence of ^{238}U and ^{234}U in secondary accumulations on grain surfaces in the sandstone bedrock. The mechanisms that may be responsible for the disequilibrium are discussed in the section of this report that deals with uranium isotopes in groundwater.

An important source of ^{226}Ra in groundwater in the confined regions of the Cambrian and Ordovician bedrock is the accumulation of nuclides of ^{238}U , ^{234}U , and ^{230}Th on the sandstone matrix due to the groundwater transport of uranyl ions. Two chemical mechanisms that remove uranyl ions from groundwater in the confined bedrock are precipitation due to a decline in the oxidation-reduction potential of the groundwater and sorption onto the surface of silicates in the sandstone bedrock. The radioactive disintegrations of ^{238}U to ^{234}Th and ^{234}U to ^{230}Th are also important mechanisms in the secondary deposition of the nuclides. The uranium nuclides disintegrate to thorium through emission of alpha particles. The recoil energy from the alpha particle emission may propel the newly formed thorium nuclides into solution from the residence sites of the uranium parent nuclides on the matrix. The

disintegration of dissolved uranium will also contribute thorium nuclides to solution. Thorium is a highly insoluble element, and ^{230}Th nuclides placed in solution by the disintegration of ^{234}U will not remain in solution. The primary mechanism by which ^{230}Th is removed from solution is the rapid sorption of the nuclides onto the sandstone bedrock. Thorium ions, because of their +4 valence, have a strong affinity for the surface of silicates in the sandstone bedrock (Stumm and Morgan, 1970).

Because of their +2 valence, radium ions are much less strongly sorbed to silicate surfaces than are either thorium ions or uranyl ions. Therefore, there is potential for desorption of ^{226}Ra formed by the disintegration of ^{230}Th on the matrix. The disintegration of ^{230}Th to ^{226}Ra is by alpha particle emission, so there is also potential for the newly formed ^{226}Ra nuclides to be physically ejected from surfaces into solution. Even if the new nuclide is not propelled into solution the disintegration energy will weaken the chemical bonds that hold the nuclide to the matrix and thus increase its potential for leaching into solution.

The desorption of ^{226}Ra from silicate surfaces is affected by the ionic strength of the groundwater. In dilute groundwaters, exchange sites on the matrix may selectively sorb radium ions out of solution. However, in more mineralized groundwater the selectivity of the matrix surface for specific ions decreases due to competition from the greater concentration of ions in solution. Therefore, as the ionic strength increases there is potential for more radium to be desorbed from the matrix.

The relation between ^{226}Ra concentration and the concentration of total dissolved minerals for 183 analyses of groundwater samples from the Cambrian and Ordovician bedrock in Illinois is shown in figure 8. The concentration of dissolved minerals is a measure of the mineralization of the groundwater and ranges from 250 to 3220 mg/L. The concentration of ^{226}Ra ranges from 0.1 to 25.0 pCi/L.

All of the ^{226}Ra concentrations of less than 2.5 pCi/L occur in groundwater that has a total dissolved mineral concentration of less than 600 mg/L. Also, all of the groundwater samples with concentrations

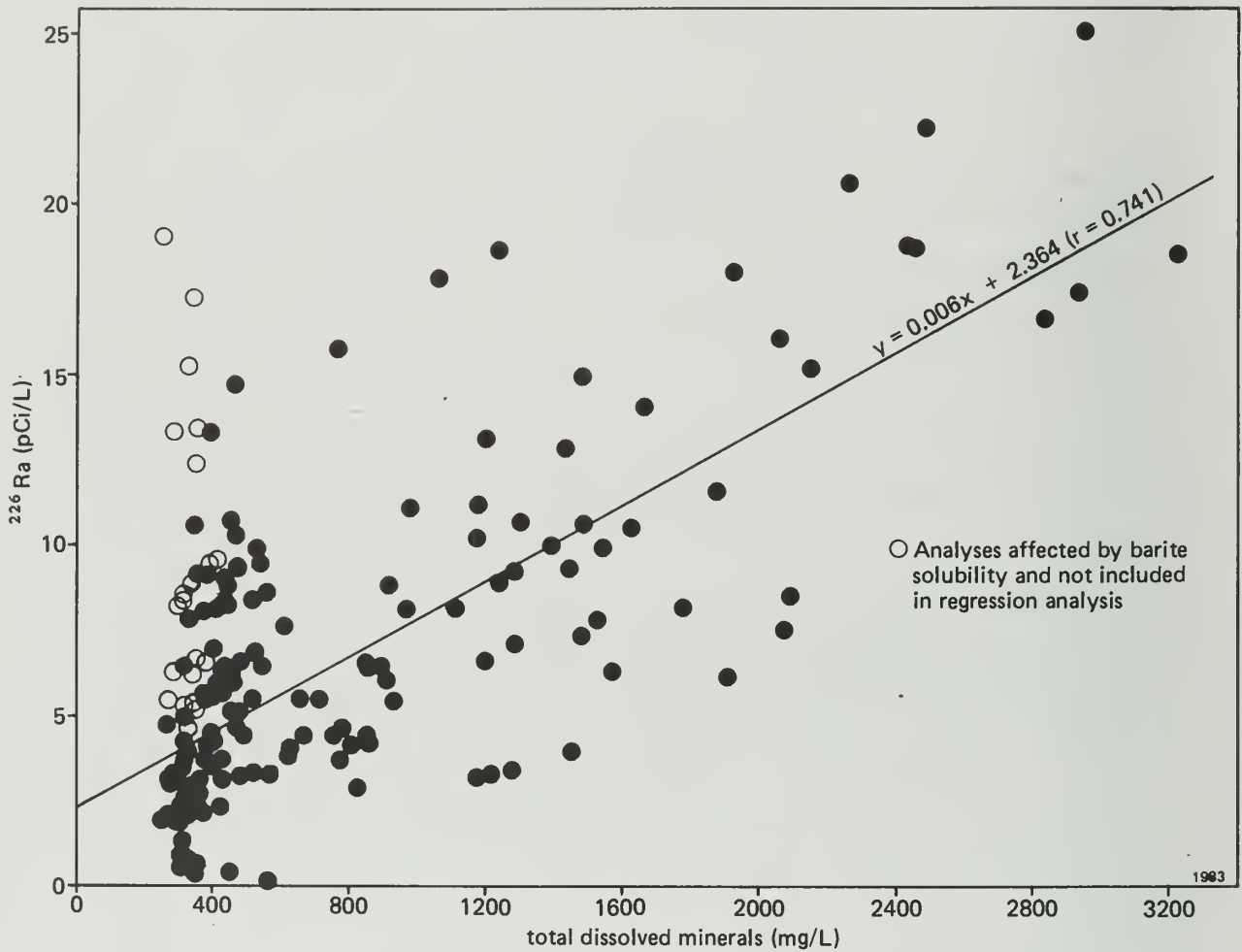


FIGURE 8. The relation between the concentration of radium-226 and total dissolved minerals in groundwater from the Cambrian and Ordovician bedrock.

of dissolved minerals greater than 1500 mg/L have ^{226}Ra concentrations greater than 6.0 pCi/L. However, many high ^{226}Ra concentrations occur in groundwater with low concentrations of total dissolved minerals.

The present research has determined that the ^{226}Ra concentrations in groundwater at some wells are controlled by precipitation-dissolution of barite (BaSO_4). The wells are in localities where it is believed that the depletion of sulfates by bacterially mediated reactions has resulted in dissolution of secondary BaSO_4 present on the aquifer matrix. ^{226}Ra analyses that are affected by barite solubility are shown with open circles on figure 8. These analyses were not included in the regression analysis. A least square line fit to the 157 analyses displayed as solid circles on figure 8, determined a correlation coefficient, r , of 0.741. The regression analysis indicates a direct relation between the ionic strength of groundwater and the concentration of dissolved ^{226}Ra . This relation was reported earlier by Emrich and Lucas (1963). The desorption of ^{226}Ra would be most significant for groundwater produced from sandstone bedrock. Unfortunately, most groundwater samples in figure 8 are from wells that produce groundwater from both sandstone and carbonate (primarily dolomite) bedrock.

Analyses at two wells in the southwestern region of the study area illustrate the importance of sorption on the sandstone bedrock to the concentration of ^{226}Ra in groundwater. Many public water supply wells in this region are constructed to produce groundwater from limestone and dolomite in the Devonian and Silurian Systems as well as from the deeper Ordovician bedrock. Groundwater in the Silurian and Devonian is under a higher hydraulic head than is groundwater in the underlying Ordovician bedrock. Therefore, during periods when a well is not pumped, groundwater flows down the open borehole from the shallow bedrock and enters the deeper units. Over time, groundwater having the chemical composition of the higher stratigraphic units displaces the native groundwater of the Ordovician bedrock in the immediate vicinity of the well. However, if the Silurian and Devonian bedrocks have a significantly lower transmissivity than does the Ordovician bedrock, then a major component of the groundwater is produced from the deeper units when the well is pumped. Municipal wells at Toulon in Stark County and Farmington

in Fulton County produce groundwater with high ^{226}Ra concentrations. However, the major ion chemical composition of groundwater produced from the wells is anomalous for the Ordovician bedrock.

Municipal well no. 1 at Toulon was constructed in 1911 with the borehole open to limestone and dolomite in the Silurian and Devonian Systems as well as to deeper stratigraphic units in the interval from the Galena Dolomite Group through the St. Peter Sandstone. The chemical analyses for this well demonstrate a change in the chemical composition of groundwater produced from the well between 1913 and 1977. The concentration of sulfate decreased from 351 to 216 mg/L, while the concentration of chloride increased from 190 to 555 mg/L and the concentration of total dissolved minerals increased from 1147 to 1690 mg/L. The variation is interpreted as indicating that with passage of time an increasing amount of groundwater produced from the well has the chemical composition of groundwater from the Silurian and Devonian. In fact, the chemical composition of groundwater analyzed from 1958 to 1977 is similar to the chemical composition of groundwater from a municipal well at Toulon constructed to produce groundwater only from the Silurian and Devonian. Although the major ion composition of groundwater produced from the two wells is similar, the concentration of ^{226}Ra in groundwater samples from the well that is open to the Ordovician ranges from 22.6 to 36.9 pCi/L, compared with 3.3 pCi/L for groundwater from the shallow well. When the deep well is pumped, a major component of groundwater is produced from the stratigraphic unit with the highest transmissivity, the St. Peter Sandstone. The groundwater from the Devonian and Silurian that has displaced the native groundwater in the Ordovician bedrock has desorbed ^{226}Ra from the surface of the bedrock matrix.

Municipal well no. 1 at Farmington was completed in 1918. The well casing extends from land surface to the top of the Galena Group. The well has an open borehole to the Galena and Platteville and the Glenwood-St. Peter. The early chemical analyses of groundwater produced from the well are typical of groundwater produced from the Ordovician bedrock for this area. However, the marked change that has occurred over the years in the chemical composition of groundwater produced from

the well indicates that groundwater from shallow stratigraphic units has entered into the Ordovician bedrock, displacing the native groundwater. In this well the casing was not pressure-grouted with cement. Therefore, groundwater from the shallow stratigraphic units may flow downward in the annular spacing between the well bore and the casing. The principal sources of the invading groundwater are limestones and dolomites in the Silurian and Devonian Systems. Additional small quantities of groundwater may be contributed from limestone in the Mississippian System and sandstone present in the Pennsylvanian System. The available chemical analyses on groundwater from this well demonstrate a marked change from 1919 to 1980; a significant part of the change occurred by 1950. The concentration of sulfate decreased from 665 to 288 mg/L, the concentration of chloride increased from 228 to 741 mg/L, and the concentration of bicarbonate increased from 278 to 702 mg/L. The concentration of calcium has decreased from 66 to 12 mg/L, magnesium has decreased from 32 to 5 mg/L, and sodium has increased from 426 to 870 mg/L. The concentration of total dissolved minerals has increased from 1620 to 2270 mg/L. The ^{226}Ra concentration of 7.5 pCi/L is high for groundwater from the shallow stratigraphic units. The invaded groundwater has evidently desorbed the ^{226}Ra from the matrix of the sandstone.

Equation (3) suggests that the residence time of groundwater in the Cambrian and Ordovician bedrock may be a significant control on the concentration of ^{226}Ra in solution. In fact, the lowest ^{226}Ra concentrations are measured in groundwater in primary recharge zones to the Cambrian and Ordovician bedrock in north-central Illinois. Away from the zone of recharge, along the direction of flow in intermediate or regional groundwater flow systems, ^{226}Ra concentrations increase. The highest concentrations are present in groundwater with long residence times where the Cambrian and Ordovician bedrock are confined. However, there are two observations that question the significance of the residence time of the groundwater on the concentration of ^{226}Ra in solution. The first observation is the occurrence of high ^{222}Rn concentrations in groundwater from the Cambrian and Ordovician bedrock in the zone of primary recharge in north-central Illinois. The high ^{222}Rn concentrations in groundwater that has very low ^{226}Ra concentrations is evidence

that ^{226}Ra is present on the aquifer matrix in the locality of the well site and that geochemical mechanisms prevent its presence in groundwater at high concentrations. The second observation is the presence of high ^{226}Ra concentrations in groundwater at the public supply wells in Toulon and Farmington that has a short residence time in the Ordovician bedrock. The increase in ^{226}Ra concentrations in the groundwater is evidence that there is an abundant source of ^{226}Ra on the matrix of the sandstone bedrock and that extraction of the ^{226}Ra from the matrix occurs rapidly. The available information indicates that residence time is not a significant control on the concentration of ^{226}Ra in groundwater. Therefore, ^{226}Ra concentrations in groundwater are not directly related to the rate of disintegration of ^{230}Th nuclides in generating nuclides of ^{226}Ra . The significant controls on the occurrence of ^{226}Ra in groundwater are geochemical mechanisms that partition ^{226}Ra between the groundwater and the matrix surfaces of the aquifer.

^{228}Ra is the first daughter nuclide in the ^{232}Th decay series. In regions where the Cambrian and Ordovician bedrock are confined, the flow rates of groundwater are very slow. Because of its short half-life (5.75 years), ^{228}Ra will not migrate significant distances in the confined groundwater from its site of generation. Therefore, the distribution of ^{232}Th in accessory minerals in the bedrock is an important control on the occurrence of ^{228}Ra in groundwater. Regional variation in the ^{228}Ra concentration in groundwater may be related to variations in the primary depositional patterns of feldspar-bearing sediments.

The highest ^{228}Ra concentration in the present set of analyses is 32.7 pCi/L for a groundwater sample collected in 1960 from a public supply well at Aurora in Kane County. The well was abandoned and sealed in 1967 because it produced highly mineralized groundwater from the Mt. Simon Sandstone; it was drilled 155 meters (510 ft) into the Mt. Simon with a total depth of 696 meters (2285 ft). Explosives were used to increase production of groundwater from the Mt. Simon. The high ^{228}Ra concentration in groundwater from the well may reflect the presence of feldspar grains in the Mt. Simon.

There is also the possibility that localities having high ^{228}Ra concentrations in groundwater may reflect secondary deposition of ^{232}Th that was transported in groundwater at ultra-trace concentrations over very long periods of time. The solubility of thorium in groundwater is discussed in the thorium section of this report.

Unlike the concentration of ^{226}Ra , the concentration of ^{228}Ra in solution is not related to the ionic strength of the groundwater. Very low ^{228}Ra concentrations are present in mineralized groundwater in the southwestern region. For example, ^{228}Ra concentrations in the public supply wells at Toulon and Farmington were 0.9 and 0.7 pCi/L, respectively. Accumulation of ^{228}Ra on the sandstone matrix is probably greatly restricted by the short half-life of the nuclide.

RADON-222 IN GROUNDWATER

^{222}Rn is a nuclide in the ^{238}U decay series that is generated by the radioactive disintegration of ^{226}Ra . ^{222}Rn has a short half-life of 3.82 days, and is a noble gas highly soluble in water. The strongly radioactive nature of this isotope is due to the short half-lives of the following four daughter nuclides in the ^{238}U decay series. A drinking water regulation for the maximum allowable concentration of ^{222}Rn has not been promulgated. A maximum contaminant level of 10,000 pCi/L for drinking water was proposed by Hess et al. (1979).

In the present research, the concentration of ^{222}Rn in groundwater was determined for 80 wells in Illinois that produce groundwater from the Cambrian and Ordovician bedrock. Duplicate samples were collected for analysis. For the majority of analyses, 10.0 ml samples of groundwater were collected with a syringe from a flowing plastic tube and injected beneath 5.0 ml of liquid scintillation fluid in a scintillation vial. The sealed samples were analyzed with the liquid scintillation technique developed by Prichard and Gesell (1977). At a small number of well sites samples of groundwater were collected and carefully sealed in 1-liter glass containers. The ^{222}Rn concentrations in these samples were determined with the emanation technique of Lucas (1977). All analyses were corrected for radioactive decay to report the concentration of ^{222}Rn present at the time of sampling.

The range in ^{222}Rn concentrations for the 80 groundwater samples is from 40 to 670 pCi/L. The concentrations are much lower than the maximum allowable concentration of 10,000 pCi/L in the proposed drinking water regulation. Figure 9 presents the relation between the ^{222}Rn concentration and the concentration of the parent ^{226}Ra isotope for 70 groundwater samples from the Cambrian and Ordovician bedrock. A regression analysis of the 70 samples determined a correlation, r , of 0.1644. Little correlation was found between the concentrations of ^{222}Rn and ^{226}Ra in the groundwater samples. Some of the highest ^{222}Rn concentrations were measured in groundwater with the lowest ^{226}Ra concentrations. However, for all of the analyses the ^{222}Rn concentrations were at least an order of magnitude greater than the ^{226}Ra concentrations. For many samples the ^{222}Rn concentrations are several orders of magnitude greater than the ^{226}Ra concentrations.

Significant factors that control the occurrence of ^{222}Rn in groundwater were reviewed by Tanner (1964A, 1980). ^{222}Rn is a soluble gas that does not react chemically. The alpha recoil disintegration process that generates ^{222}Rn may break or weaken the chemical bonds that hold the ^{226}Ra parent isotope onto the solid matrix. The momentum from the alpha recoil will directly propel a portion of the newly formed ^{222}Rn nuclides into solution. Because of its short half-life and the slow velocity of groundwater in the Cambrian and Ordovician bedrock, dissolved ^{222}Rn cannot occur at significant distances from its site of generation. Also, the concentration of ^{222}Rn in groundwater due to diffusion of the isotope from the interior of the rock matrix will be very slight because of the short half-life. The significant source of ^{222}Rn in groundwater of the Cambrian and Ordovician bedrock is the presence of the ^{226}Ra parent on the surface of the aquifer matrix in the immediate vicinity of the well site. The measured ^{222}Rn concentrations in groundwater are evidence that ^{226}Ra is ubiquitous on the matrix of the Cambrian and Ordovician bedrock, even in regions where the concentration of ^{226}Ra in groundwater is very small. Geochemical mechanisms that may partition ^{226}Ra onto the matrix are discussed in the radium isotope section of this report. The mechanisms include cation-exchange and coprecipitation with iron, calcium, magnesium, or barium to form mineral phases. ^{222}Rn generated by disintegration of ^{226}Ra present on the matrix

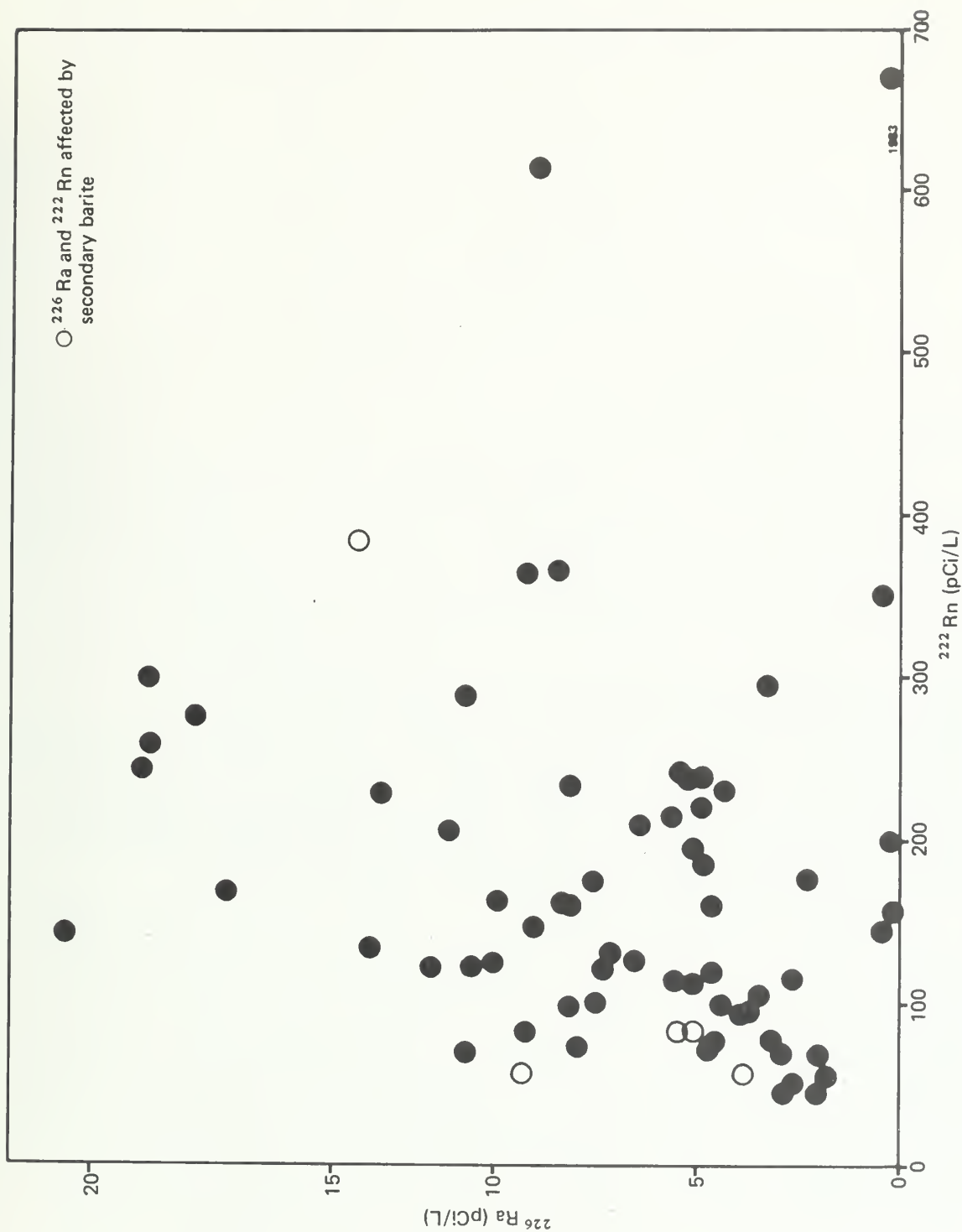


FIGURE 9. The low correlation coefficient between the concentrations of radium-226 and radon-222 in groundwater from Cambrian and Ordovician bedrock. For a least square line fit to the analyses, the correlation coefficient, r , = 0.164.

would be efficiently released by these mechanisms to groundwater, with one exception. Precipitates of barite do not release ^{222}Rn generated by disintegration of coprecipitated ^{226}Ra (Hahn, 1936). Some anomalously low and anomalously high ^{222}Rn concentrations measured in groundwater from wells in northeastern Illinois are attributed to secondary accumulations of barite on the rock matrix of the well bore. At these wells low concentrations of ^{222}Rn and ^{226}Ra in groundwater were measured during periods when extreme supersaturation of barium and sulfate ions in solution resulted in secondary precipitation of barite. High concentrations of ^{226}Ra and ^{222}Rn in groundwater were measured at these wells during periods of dissolution or corrosion of the barite.

URANIUM ISOTOPES IN GROUNDWATER

The two isotopes of uranium that may occur naturally at significant concentrations in groundwater are ^{238}U and ^{234}U . Both isotopes are members of the ^{238}U decay series (fig. 5). The U.S. Environmental Protection Agency has not promulgated a maximum contaminant level for uranium in water. A very preliminary study that applied the criteria used to determine the drinking water regulations for ^{226}Ra indicated that a maximum contaminant level for uranium in groundwater would be approximately 10 pCi/L (C. Richard Cothorn, United States Environmental Protection Agency, personal communication). However, the element was excluded from the National Interim Primary Drinking Water Regulations because uranium is both chemically and radiologically toxic.

Analyses for ^{234}U and ^{238}U were performed on groundwater samples collected from 130 wells in Illinois that produce groundwater from the Cambrian and Ordovician bedrock. Nineteen-liter (5-gallon) samples of groundwater were collected at the wells and acidified with nitric acid to a pH of 1. The laboratory analytical methods are described in Osmond and Cowart (1976). Both filtered (0.22 micron pore size membrane) and unfiltered samples were collected at many wells located widespread across the study area to evaluate the effect of particulate matter in groundwater on the measured concentration of the two nuclides. The results on the filtered and unfiltered samples were identical within the statistical limits of accuracy for the analytical method.

The mass concentration of uranium in the 130 groundwater samples ranged from less than 0.002 $\mu\text{g/L}$ to 1.10 $\mu\text{g/L}$; the combined activity concentration of ^{234}U and ^{238}U in the samples ranged from less than 0.1 pCi/L to 7.9 pCi/L. For the majority of analyses (95 samples) the combined concentrations were less than 2.0 pCi/L. The combined concentrations were greater than 3.0 pCi/L in 11 samples and the combined concentrations exceeded 5.0 pCi/L in only 3 samples. All of the combined activity concentrations greater than 1.0 pCi/L were present in groundwater that had marked enrichment in ^{234}U .

Dissolved uranium species are very sensitive to the oxidation-reduction potential of groundwater. Uranium occurs as the mobile hexavalent ion (usually as uranyl) in oxidizing environments and as the highly insoluble quadrivalent ion in reducing environments. Uranium (as uranyl complexes) may migrate away from the primary source and be emplaced in secondary accumulations. Precipitation of uranium at reducing barriers in groundwater flow systems is a mechanism responsible for the formation of some economic uranium deposits in sandstones (Hostetler and Garrels, 1962).

Figure 10 presents the relation between Eh and uranium concentration in groundwater for 77 wells in the study area that produce groundwater from the Cambrian and Ordovician bedrock and for 5 wells that produce groundwater from shallower aquifers. The data indicate that the oxidation-reduction potential is an important control on the uranium concentration in groundwater. Dissolved uranium concentrations were less than 0.08 $\mu\text{g/L}$ in all groundwater samples in which Eh values were -50 millivolts or lower. The highest uranium concentrations are present where Eh values were +100 millivolts or greater. Many groundwater samples with Eh values between -50 to +50 millivolts have appreciable uranium concentrations. It is important to note that the wells have boreholes that are open to several stratigraphic units; groundwater from discrete units may differ markedly in dissolved sulfide concentrations, oxidation-reduction potential, and uranium concentration. The sensitivity of Eh values measured with the platinum electrode method to the presence of sulfide in groundwater is discussed in an earlier section of this report.

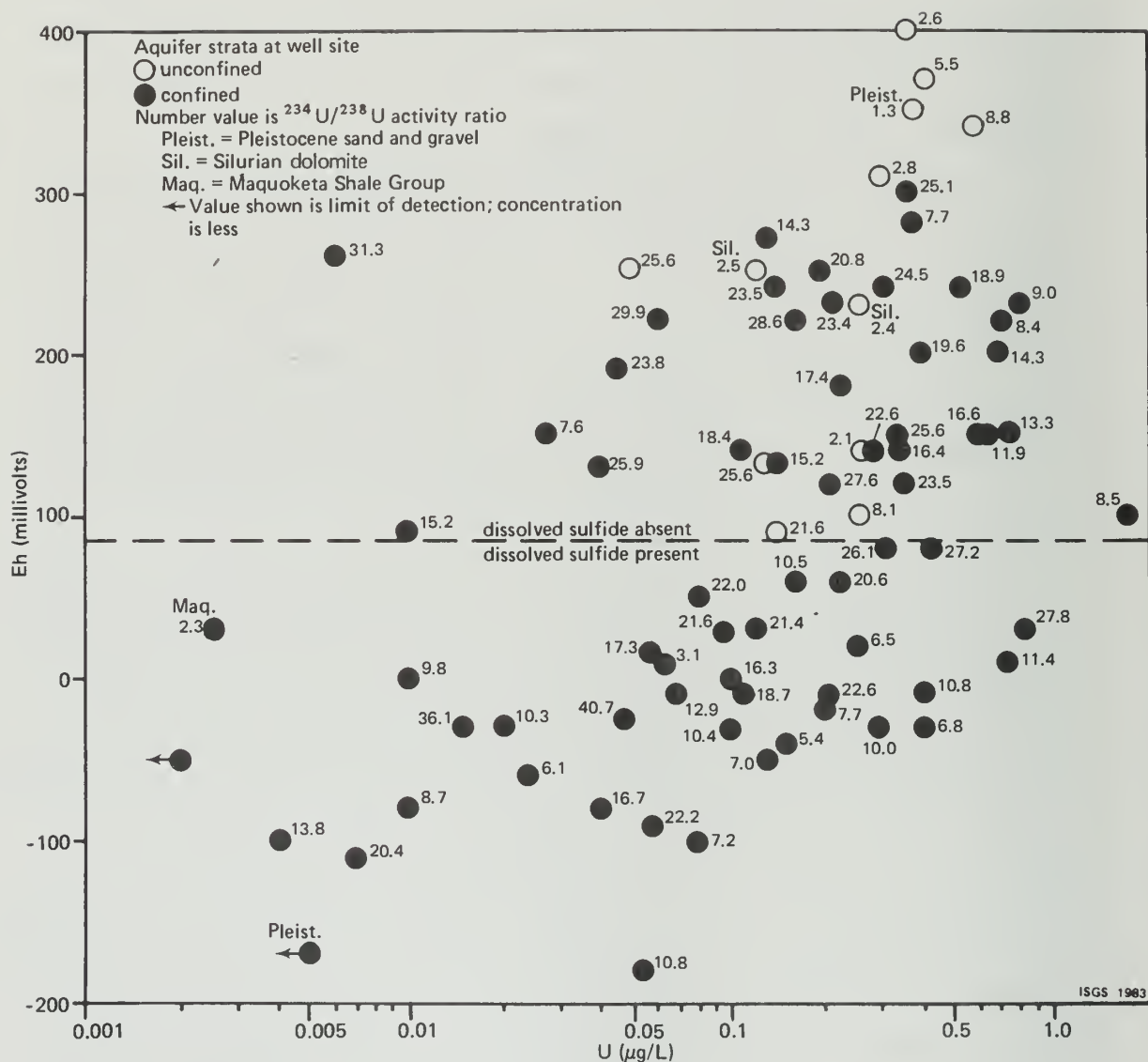


FIGURE 10. The relation between Eh (platinum electrode) and the concentration of uranium in groundwater from the Cambrian and Ordovician bedrock. The $^{234}\text{U}/^{238}\text{U}$ activity ratio is shown for each analysis. A few analyses are listed for groundwater from other aquifers.

Figure 10 presents the value for the $^{234}\text{U}/^{238}\text{U}$ activity ratio with the analyses. The ratios range from 2.4 to 40.7 for the analyses on groundwater from the Cambrian and Ordovician bedrock and from 1.3 to 2.5 for the analyses on groundwater from shallower aquifers. For all of the analyses, there is no relation between the activity ratio and either the uranium concentration or the Eh of groundwater.

Disequilibrium in the natural environment between ^{234}U and ^{238}U was first reported in 1955 (Cherdyntsev et al., 1955). From a review of the literature, Osmond and Cowart (1976) found that research has documented the disequilibrium in a wide range of materials and environments. Most waters are found to have disequilibrium between the activities of ^{234}U and ^{238}U . The dissolved uranium in surface waters is usually enriched in ^{234}U ; ratios of the activity of ^{234}U to ^{238}U as great as 6.4 have been reported for small streams. The ocean has about 15 percent more ^{234}U than ^{238}U . The uranium isotopic abundances and the disequilibrium between them may vary widely in groundwater; reported values for activity ratios range from as low as 0.5 to as high as 12.3.

The widespread and extreme disequilibrium between ^{234}U and ^{238}U that occurs in groundwater from the Cambrian and Ordovician bedrock of the study area is unique. The high activity ratios have not been found in other flow systems.

The $^{234}\text{U}/^{238}\text{U}$ activity ratios in groundwater from the Cambrian and Ordovician bedrock do indicate regional patterns. The lowest activity ratios (values less than 3.0) were measured in the north-central and northwestern part of the study area in zones of primary recharge where the Pennsylvanian System and the Maquoketa Group are absent and groundwater has had a short residence time in the bedrock. With increasing distance along flow paths from the point of recharge there is an increase in the activity ratio, and values greater than 20 occur widely in the study area. The highest activity ratios are present in the northeastern, northwestern, and east-central parts of the study area where the Cambrian and Ordovician bedrock are confined. An interesting feature are the relatively low $^{234}\text{U}/^{238}\text{U}$ activity ratios in confined groundwater in the southwestern region of the study area. The activity ratios range from 5.4 to 14.8 and are commonly less than 10 over the central and southern

part of the region.

The genesis of the extreme enrichment of ^{234}U in groundwater of the Cambrian and Ordovician is not well understood at the present time. The high activity ratios may be due to interaction of geochemical and radiological mechanisms. It is also important to consider geologic processes that may have supplied uranium to the groundwater flow system.

Rosholt et al. (1963) advanced the concept that the recoil from the $^{238}\text{U} \rightarrow ^{234}\text{Th}$ alpha particle decay event may place the subsequently formed ^{234}U nuclide (^{234}Th and ^{234}Pa have short half-lives) in an environment that would favor a +6 valence; in fact, self-oxidation may occur as a result of electron stripping during the $^{234}\text{Th} \rightarrow ^{234}\text{Pa} \rightarrow ^{234}\text{U}$ decay events. The higher valence state would enhance dissolution of ^{234}U into groundwater.

Kigoshi (1971) demonstrated through experimentation that direct recoil of the ^{234}Th nucleus (from ^{238}U decay) into solution could occur. The short-lived ^{234}Th decays to ^{234}U , thereby enriching the groundwater in ^{234}U while depleting the surface of the aquifer matrix. A large number of the recoiling nuclei pass through the groundwater in the open pore spaces to become embedded in adjacent grains of the aquifer matrix, leaving fission tracks open to the surface (Huang and Walker, 1967). Fleischer (1980) experimented with natural minerals (mica, feldspar, quartz, and obsidian) to investigate the release of embedded nuclei as a result of the etching of fission tracks by solutions. An important finding of the study was that all of the solutions (including deionized water) would leach a significant portion of the embedded nuclei from all of the minerals.

Kronfeld (1974) advanced ^{234}Th alpha-recoil as the mechanism responsible for the generation of $^{234}\text{U}/^{238}\text{U}$ activity ratios as high as 12 in groundwater from a confined sandstone aquifer in Texas. Kronfeld proposed that the effectiveness of the alpha-recoil mechanism was enhanced by the presence of a diffuse precipitate of secondary uranium on the sandstone matrix.

Disintegration events that weaken chemical bonds or propel nuclides into solution and solution etching of fission tracks may all be

mechanisms that are important in the enrichment of ^{234}U in groundwater from the Cambrian and Ordovician bedrock in the study area. The transport of ^{234}U and ^{238}U in regional groundwater flow systems with secondary accumulation on the sandstone bedrock is thought to be important to the presence of high concentrations of ^{226}Ra in groundwater. The widespread occurrence of high $^{226}\text{Ra}/^{228}\text{Ra}$ activity ratios in groundwater from the Cambrian and Ordovician bedrock (fig. 7) is evidence of the presence of secondary uranium on the sandstone bedrock.

In the present report the authors are suggesting a new concept: that secondary uranium and possibly the extreme enrichment in ^{234}U in groundwater may be significantly related to glacial processes. Research by Perry, Grundl, and Gilkeson (1982) established that the isotopic composition of the water molecule is evidence of the importance of glacial processes to the recharge of groundwater to the Cambrian and Ordovician bedrock where these units are confined by the Maquoketa Shale Group and/or the Pennsylvanian System. Gilkeson, Perry, and Cartwright (1981) advanced a glacial recharge mechanism to explain the anomalous isotopic composition of both the water molecule and the dissolved sulfate present in groundwater of the Cambrian and Ordovician bedrock in the northeastern, southeastern, and southwestern regions of the study area.

The mechanisms of recharge related to glacial processes is not clearly understood. As a result of the geothermal gradient, as well as the heat generated by friction, meltwater was present at the base of the continental glaciers (Weertman, 1972; Clayton and Moran, 1974; Freeze and Cherry, 1979). It is postulated that pressure from the glacial ice overburden caused basal meltwater to recharge into the Cambrian and Ordovician bedrock. It is important to consider that these glacial recharge events were repeated with the numerous advances of continental ice sheets into Illinois during the Pleistocene. The pulverizing of uranium-bearing rocks to very fine particles by glaciers would increase the availability of uranium for dissolution. The concept advanced in the present report is that the dissolved uranium extracted from the finely ground sediments into the basal meltwater was enriched in ^{234}U that was more mobile because of its radiogenic origin.

However, the extent of preferential dissolution of ^{234}U in glacial environments has not been established. Analyses on uranium isotopes in glacial materials are limited. A few analyses by Rosholt, Doe and Tatsumuto (1966) determined that glacial tills were greatly depleted in ^{238}U as compared with ^{232}Th and also depleted in ^{234}U as compared with ^{238}U . Additional analyses on glacial sediments and glacial meltwaters are necessary to confirm the extraction of uranium with preferential extraction of ^{234}U .

The regional distribution of $^{234}\text{U}/^{238}\text{U}$ activity ratios in groundwater of the Cambrian and Ordovician bedrock in the study area is compatible with the idea that glacial processes are involved in generation of the disequilibrium. The highest activity ratios (values from 25 to 40) occur in the eastern part of the study area where groundwater would have been recharged during the Wisconsinian by the most recent glacial advances. Wisconsinian glaciers did not advance over the southwestern region of the study area. The low activity ratios (values from 5 to 11) in groundwater of the Ordovician bedrock in the southwestern region may reflect recharge by an earlier glacial advance. The activity ratio diminishes over time as the excess ^{234}U disintegrates. It is possible that groundwater in the Cambrian and Ordovician bedrock in the southwestern region is quite old, and that recharge was due to a glacial advance during the Illinoian.

THORIUM ISOTOPES IN GROUNDWATER

The immediate parent nuclides of all four natural radium isotopes are isotopes of the element thorium. However, the concentration of thorium ions in solution is insignificant; the source for the radium isotopes in groundwater is the disintegration of thorium isotopes present either in accessory minerals in the aquifer matrix or as secondary accumulations on the aquifer matrix.

In the present research, alpha pulse height analyses for ^{232}Th (the parent nuclide for ^{228}Ra) and ^{230}Th (the parent nuclide for ^{226}Ra) were performed on groundwater samples from seven wells that produce groundwater from the Cambrian and Ordovician bedrock. Groundwater from the seven wells exhibits a large variation in radium concentrations;

^{226}Ra concentrations range from 0.3 to 15.9 pCi/L and ^{228}Ra concentrations range from 2 to 13 pCi/L. The thorium species were concentrated from separate 19-liter (5-gallon) samples of unfiltered and filtered (0.22 micron pore size membrane) groundwater collected from each well. The analysis did not detect ^{232}Th or ^{230}Th in any of the samples. The limit of the analytical method is 0.01 $\mu\text{g/L}$ expressed as ^{232}Th .

Thorium ions, which have a +4 valence state, have extremely slight solubilities. Thorium present in groundwater is probably restricted to ultratrace concentrations transported as complexed species (Herman and Langmuir, 1978). Organic materials may act as an agent for complexation. The transport of thorium species in groundwater flow systems in the Cambrian and Ordovician bedrock is unknown at the present time. Of primary interest is the role of transport of ^{232}Th as complexed species on the high concentrations of ^{228}Ra that occur in some localities in the northeastern and east-central regions of the study area. Because of the long half-life of ^{232}Th , it is possible that transport of ultratrace concentrations over long periods of geologic time may result in significant concentrations in zones of secondary accumulation. The secondary accumulation of ^{232}Th may have occurred earlier in geologic time when thorium was transported in the Cambrian and Ordovician bedrock by brines that contained organic material. The transport of ^{230}Th to the concentration of ^{226}Ra in groundwater is thought to be insignificant because of the short half-life of the nuclide.

BARIUM IN GROUNDWATER

BACKGROUND

Barium concentration in untreated groundwater from a large number of wells in Illinois exceeds the drinking water standard of 1.0 mg/L (U.S. EPA, 1975). The largest area where the groundwater exceeds the standard is in northeastern Illinois. In this area of northeastern Illinois and in more restricted settings of northern Illinois, high-barium groundwater is produced from bedrock aquifers of the Cambrian and Ordovician Systems. Outside northern Illinois, high barium concentrations occur in groundwater from less productive aquifers in isolated locations.

Gilkeson et al. (1978) established that: (1) the concentration of dissolved sulfate in groundwater is an important control on the concentration of dissolved barium because of the low solubility of the mineral barite (BaSO_4); (2) the high barium concentrations occur in groundwater that is anomalously depleted in dissolved sulfate; (3) the high barium concentrations occur in confined aquifers; and (4) the high dissolved barium concentrations occur within anaerobic environments or downgradient these environments.

Gilkeson, Perry, and Cartwright (1981) interpret the depletion of dissolved sulfate is due to bacterially mediated reactions occurring in anaerobic environments. Characteristics of the groundwater that support this interpretation are the presence of hydrogen sulfide, increased alkalinity, and enrichment of the heavy sulfur isotope (^{34}S) in the residual dissolved sulfate.

The source for dissolved sulfate in groundwater from the Cambrian and Ordovician bedrock of northeastern Illinois where the bedrock is confined by the Maquoketa Shale Group is problematic. Stable isotope analyses have established that the sulfate molecule is of a different geologic age than the Cambrian or Ordovician (Perry, Grundl, and Gilkeson, 1982). Gilkeson, Perry, and Cartwright (1981) have suggested that the sulfates are derived from evaporites of a younger geologic age and were recharged to the Cambrian and Ordovician bedrock as a result of glacial

processes. Prior to the glacial recharge events, groundwater in the Cambrian and Ordovician sandstone bedrock may have had low sulfate concentrations and high concentrations of barium. Feldspars present as accessory minerals in the sandstone bedrock may have been the source of barium. The interaction between an invaded groundwater with high concentrations of sulfate and a native groundwater with high concentrations of barium resulted in secondary precipitation of barite on the aquifer matrix. At the present time, within localities where strong anaerobic conditions exist, the sulfates have been consumed by microbial reactions. With depletion of the sulfates, barium concentrations are not controlled by the solubility of barite and may be present at significantly higher concentrations.

BARIUM IN GROUNDWATER FROM BEDROCK OF THE CAMBRIAN AND ORDOVICIAN SYSTEMS IN NORTHEASTERN ILLINOIS

Figure 11 shows the distribution of sulfate, and figure 12 the distribution of barium, in groundwater from municipal wells in a region in northeastern Illinois that produce groundwater from the Cambrian and Ordovician bedrock. Analyses providing data for figures 11 and 12 were performed on groundwater samples from wells open to the Ironton-Galesville Sandstone; a few of the wells were open only to the Ironton-Galesville but most of the wells were also open to other stratigraphic units in the Cambrian and Ordovician Systems. The samples analyzed were collected during periods of large withdrawals of groundwater from each well. Figure 11 indicates that over a large area of northeastern Illinois the dissolved sulfate concentration is less than 10 mg/L. East and southeastward from this area the dissolved sulfate concentration increases rapidly and is present at concentrations greater than 800 mg/L in southeastern Cook County. Figure 12 shows that over a large part of McHenry and Kane Counties, the northeastern and central part of De Kalb County, the western part of Lake County, the northwestern part of Cook County, and the northwestern part of Du Page County, groundwater produced from wells open to the Cambrian and Ordovician bedrock exceeds the EPA drinking water limits of 1.0 mg/L for barium. At many wells the dissolved barium concentration exceeds 10 mg/L. At a few wells the

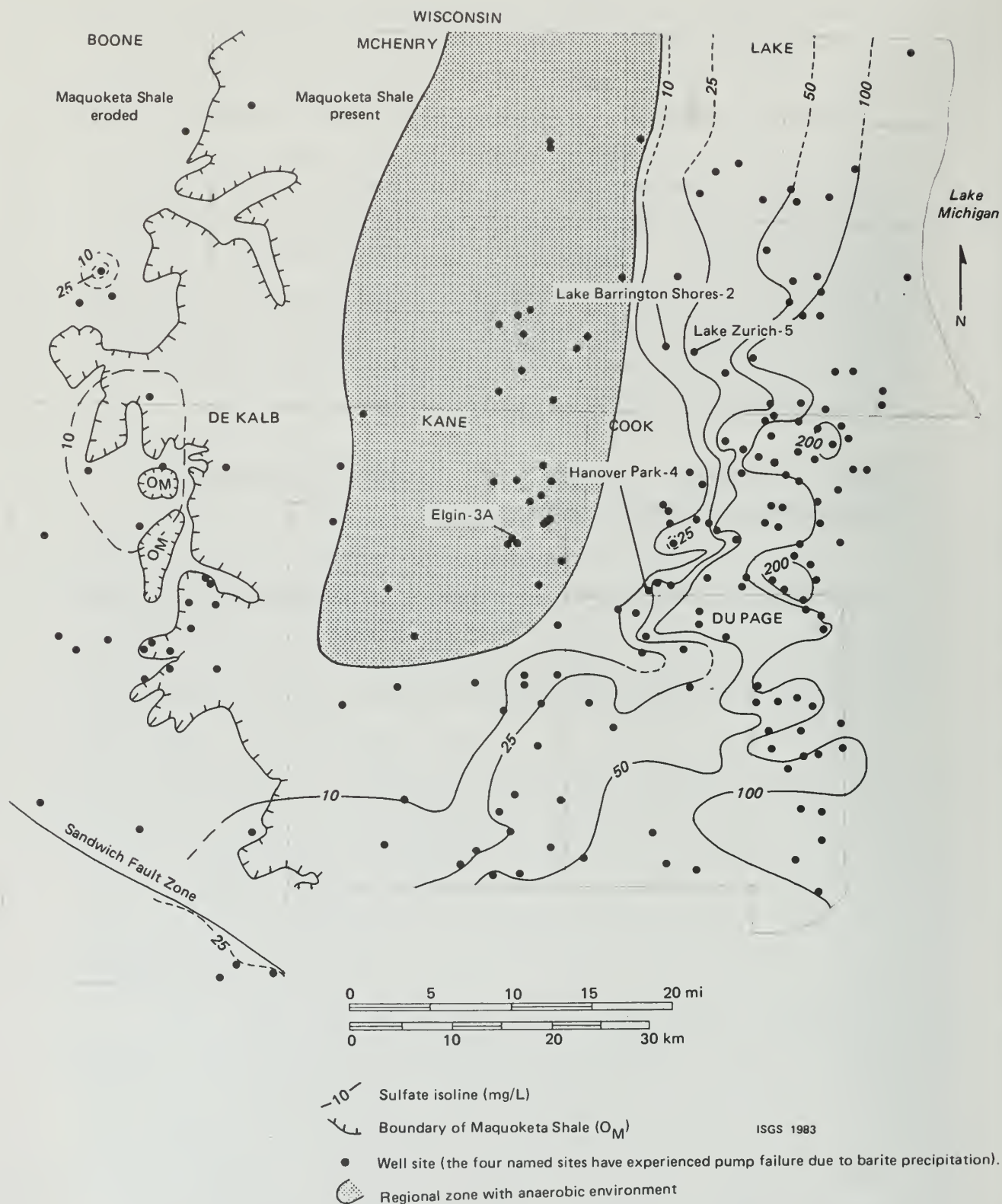


FIGURE 11. The distribution of dissolved sulfate in groundwater from the Cambrian and Ordovician bedrock for a region of northeastern Illinois (the Ironton-Galesville Sandstone is the principal aquifer).



FIGURE 12. The distribution of dissolved barium in groundwater from the Cambrian and Ordovician bedrock for a region of northeastern Illinois (the Ironton-Galesville Sandstone is the principal aquifer).

dissolved barium concentration is greater than 20 mg/L.

Barium concentrations were determined for unfiltered and filtered (0.22 micron pore size membrane) untreated groundwater samples collected at many wells. The effect of the filtration on barium concentrations was insignificant, even for groundwater having the highest barium concentrations. The barium in groundwater pumped from the wells was in solution; very little was present as particulate matter.

A comparison of figures 11 and 12 shows the important relation between the concentration of sulfate and the concentration of barium in groundwater. Where the rapid increase in sulfate concentration in groundwater occurs (in the eastern and southern part of the region), there is a rapid decline in barium concentration. The two figures can be used as a basis for making decisions concerning the siting of high-capacity wells to produce groundwater from the Cambrian and Ordovician bedrock.

In northeastern Illinois, the highest dissolved barium concentrations are present in a locality in which there is a strong anaerobic environment in the Cambrian and Ordovician bedrock due to confinement by the Maquoketa Shale Group. Over a large part of Boone and De Kalb Counties, the Maquoketa is absent and low barium concentrations occur in groundwater from the Cambrian and Ordovician bedrock that has a high Eh. However, at a location in central De Kalb County where the Maquoketa is absent, dense, unfractured dolomites of the Galena and Platteville Groups confine the underlying bedrock, and concentrations of barium greater than 1.0 mg/L are present in groundwater, having a low Eh, that is produced from the St. Peter Sandstone and from the Iron-ton-Galesville Sandstone.

In addition to the regional variation in barium and sulfate in groundwater from wells finished in the Cambrian and Ordovician bedrock (figs. 11 and 12), a marked variation in barium and sulfate may also occur in groundwater produced from different stratigraphic units open to the borehole at a specific well site. An objective of the present research was to identify the stratigraphic units of the Cambrian and Ordovician Systems that produce groundwater with high barium concentrations.

If the source of the barium is groundwater from discrete intervals of relatively nonproductive bedrock that are open to the borehole, then the cemented casing used in well construction to prevent production of groundwater from the discrete units would lower the concentration of barium in groundwater produced from the well. Data gathered in this study have established that the high dissolved barium concentrations occur in groundwater from the more productive aquifers in the Cambrian and Ordovician bedrock—the St. Peter Sandstone and the Ironton-Galesville Sandstone. In fact, groundwater from the Ironton-Galesville, regionally the most productive aquifer, has the highest dissolved barium concentrations. Because of the high barium concentrations that occur in groundwater in the more productive bedrock, design features (cemented casing) do not have a significant effect on lowering barium concentrations in groundwater produced from high capacity wells. Specific examples of this general finding are presented in the following discussion.

A test well for the community of Sleepy Hollow in Kane County was initially constructed to produce groundwater only from the St. Peter. Analysis of a sample collected during a production test determined a barium concentration of 13.2 mg/L for groundwater from the St. Peter. The test well was then deepened and constructed to produce groundwater only from the Ironton-Galesville. Analysis of a groundwater sample collected from the Ironton-Galesville during a production test determined a barium concentration of 18.2 mg/L.

Additional examples of wells constructed to produce groundwater only from the Ironton-Galesville that produce groundwater with a barium concentration greater than the drinking water regulation of 1.0 mg/L are Carol Stream-5 (Du Page County), with a barium concentration of 4.4 to 4.9 mg/L; Bloomingdale-8 (Du Page County), with a barium concentration of 3.5 mg/L; and Cary-6 (McHenry County), with a barium concentration of 8.0 mg/L. Examples of wells that produce groundwater with high barium concentrations and are constructed with cemented casing from the surface downward through the St. Peter to produce groundwater mainly from the Ironton-Galesville (with a small contribution from the Eminence Formation, the Potosi Dolomite, and the Franconia Formation)

are: Crystal Lake-6 (McHenry County), with a barium concentration of 10.2 mg/L; Crystal Lake-8 (McHenry County), with a barium concentration of 16.0 mg/L; and Cary-4 (McHenry County), with a barium concentration of 4.2 mg/L.

Analyses of groundwater from municipal wells located in two well fields at Elgin in Kane County indicate that the highest dissolved barium concentrations are present in groundwater from the Ironton-Galesville. Municipal wells at Elgin are constructed with uncased boreholes to receive groundwater from a large section of bedrock. All of the wells are open to stratigraphic units from the Galena downward through the Ironton-Galesville. In addition, several wells at Elgin are also open to the Eau Claire Formation and the upper part of the Mt. Simon Sandstone. The wells at Elgin that produce groundwater with the highest dissolved barium concentrations were developed with explosives to increase production of groundwater from the Ironton-Galesville. Examples are Elgin-6, with a barium concentration ranging from 16.7 to 22.4 mg/L, and Elgin-5A, with a barium concentration of 18.2 mg/L. Lower barium concentrations occur in groundwater from municipal wells at Elgin that were not developed with explosives and therefore produce a smaller component of groundwater from the Ironton-Galesville. Examples are groundwater samples collected from Elgin-4A, with a barium concentration of 8.4 mg/L, and Elgin-5, with a barium concentration of 7.6 mg/L. Note that groundwater from Elgin-5 and Elgin-6 have significantly different barium concentrations. The wells are only 198 meters (650 ft) apart and have open boreholes to the same stratigraphic units. The significant difference between the two wells is that explosives were used in Elgin-6 to increase the production of groundwater from the Ironton-Galesville.

Three well sites located in central De Kalb County illustrate the variation in barium present in groundwater from different stratigraphic units of the Cambrian and Ordovician Systems. A groundwater sample from a well located at Donny Brooks Estates constructed with an open borehole to stratigraphic units from the Galena through the St. Peter has a barium concentration of 0.13 mg/L. A groundwater sample from a well at Kishwaukee College constructed with the borehole open

only to the Glenwood-St. Peter has a barium concentration of 1.4 mg/L. In central De Kalb County, groundwater with the highest barium concentration (1.0 to 2.3 mg/L) was collected from a well at the village of Malta that has an open borehole to stratigraphic units from the Glenwood-St. Peter through the Ironton-Galesville. Groundwater samples with the highest barium concentrations were collected from this well during periods of extensive pumpage when a larger component of groundwater was produced from the Ironton-Galesville.

Municipal wells at De Kalb, Illinois in De Kalb County are an additional example of the occurrence of higher barium concentrations in groundwater from the Ironton-Galesville. The municipal wells are constructed with an open borehole to stratigraphic units from the Glenwood-St. Peter through the Ironton-Galesville. Two municipal wells developed with explosives in the Ironton-Galesville have slightly higher barium concentrations than wells not developed with explosives. The two wells developed with explosives are De Kalb-6, with a barium concentration of 1.8 mg/L, and De Kalb-4, with a barium concentration of 1.4 mg/L. The concentration of barium in groundwater from four municipal wells at De Kalb not developed with explosives ranges from 0.3 to 1.0 mg/L.

A laboratory experiment (Sillen and Martell, 1964) has determined the solubility product constant for barite to be $10^{-10.0}$. The solubility product for barite can also be calculated from thermodynamic data. The value was determined to be $10^{-8.9}$ (Gilkeson et al., 1978) from calculations with thermodynamic values from Garrels and Christ (1965). Refined values for the thermodynamic properties of elements and minerals were presented by Robie, Hemingway, and Fisher (1978). The solubility product for barite, determined with the refined thermodynamic data, is $10^{-9.97}$ —a value identical to the solubility product determined by laboratory experiment.

The relation of the activities of barium ion (Ba^{2+}) and sulfate ion (SO_4^{2-}) in samples of untreated groundwater collected from selected wells finished in bedrock of the Cambrian and Ordovician Systems in northern Illinois is shown in figure 13. The activities (thermodynamically effective concentrations) were calculated from the analytical concentrations of barium and sulfate in groundwater samples by using

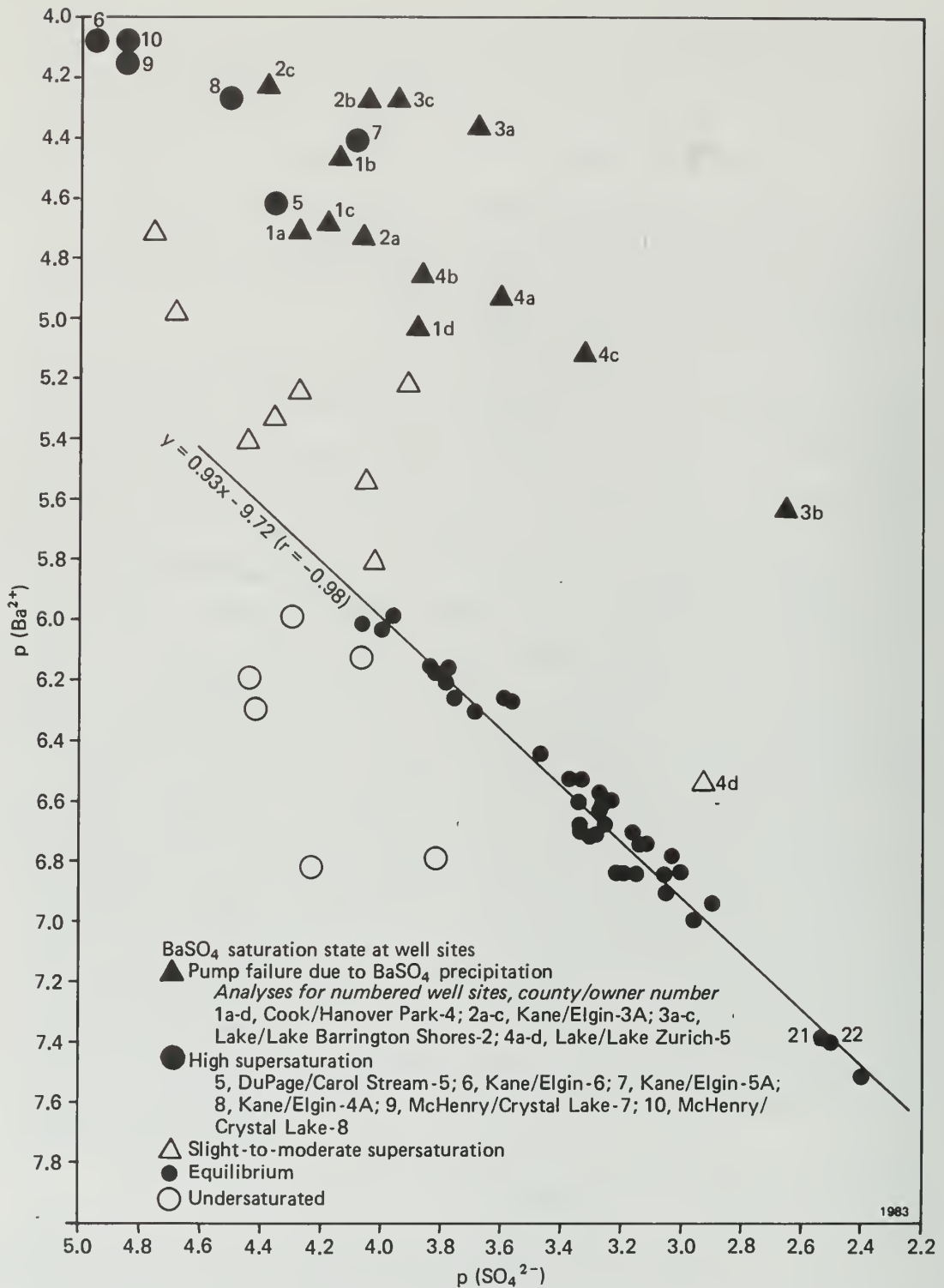


FIGURE 13. The relation of the activities of (Ba^{2+}) and (SO_4^{2-}) in groundwater from the Cambrian and Ordovician bedrock to the solubility of BaSO_4 .

the extended form of the Debye-Hückel equation. The procedure for performing calculations with the Debye-Hückel equation is given in Hem (1970). The analyses presented in figure 13 are divided into five sets. One set of 40 samples (displayed as small dots) collected from well sites widely distributed in northern Illinois shows a strong linear trend on the log-log plot. A linear regression line was fit to the 40 analyses with a correlation coefficient, r , of -0.98. The means of the solubility products of the 40 samples is $10^{-9.95}$ with a standard deviation of ± 0.08 . This value is essentially identical to the solubility product of barite determined by laboratory experiment or by calculation with the refined thermodynamic data (Robie et al, 1978). The activities of (Ba^{2+}) and (SO_4^{2-}) in the 40 analyses located along the linear regression line in figure 13 are interpreted to be in equilibrium with the mineral phase barite.

Six analyses (displayed as open circles) in figure 13 that plot a significant distance below the solubility product line represent a set of groundwater samples that are undersaturated with respect to barite. This interpretation is supported by the fact that the groundwater samples in the set are from wells located in north-central Illinois that have short flow paths for groundwater from the point of recharge. The low (Ba^{2+}) activities are due to the short residence time of the groundwater or to a limited source of barium in the aquifer matrix and thus have not reached saturation.

The groundwater samples on figure 13 that plot a significant distance above the solubility product line are supersaturated with respect to barite. All of the groundwater samples that have barium concentrations greater than 1.0 mg/L are part of this set. The supersaturation is a result of the mixing of groundwater with different chemical compositions in the open well bore. Figure 13 presents multiple analyses (displayed as solid triangles) from four well sites where expensive rehabilitation was necessary because of precipitation of barite in the pump. The analyses indicate that there is a variation in the degree of supersaturation depending upon the pumping schedule of the individual wells. The figure also presents analyses from several wells (displayed as large solid dots) where there is a high degree of supersaturation

but well failure has not occurred to the present time. There is potential for barite precipitation to occur at these wells; the precipitation may result in failure of the wells.

CASE HISTORIES—PUMP FAILURES DUE TO SECONDARY PRECIPITATION OF BARIUM SULFATE

At four wells in northeastern Illinois expensive maintenance has been necessary because of barite precipitation in the well bore, pump and discharge pipe. The four wells are Hanover Park-4 in Cook County, Elgin-3A in Kane County, and Lake Zurich-5 and Lake Barrington Shores-2 in Lake County. All four wells are constructed with the borehole open to stratigraphic units from the Galena Dolomite Group through the Ironton-Galesville Sandstone. The boreholes extend a short distance into the Eau Claire Formation. The purpose of drilling a short distance into the shale and dolomite of the Eau Claire is not to produce groundwater from the formation but to provide a reservoir for loose bedrock that sloughs off of the borehole over time.

At the four wells discrete rock units are contributing groundwater of markedly different chemical compositions to the well, and therefore, the chemical composition of groundwater discharged from the wells is related to the pumpage schedule. During periods of extensive withdrawals a larger component of groundwater is produced from the Ironton-Galesville Sandstone, the most productive unit, and this is reflected in an increase in barium concentration in the groundwater. Large withdrawals of groundwater from the Cambrian and Ordovician bedrock in northeastern Illinois have resulted in the stratigraphic unit with the highest transmissivity, the Ironton-Galesville, having a lower hydraulic head than the overlying and underlying bedrock. During periods when wells are not pumped, there is a cross-formational flow of groundwater in the open borehole in response to differences in hydraulic head between the formations. The lower head in the Ironton-Galesville results in recharge of groundwater to the Ironton-Galesville from overlying bedrock in the open borehole. If the well is also open to the underlying Eau Claire or to the Mt. Simon, then groundwater will flow up the open borehole from these stratigraphic units and into

the Ironton-Galesville during periods of nonpumpage. As a result of this cross-formational flow the native groundwater of the Ironton-Galesville may be a small component of the groundwater produced from a well pumped only intermittently for short periods of time. The chemical analyses presented in figure 13 for each of the four wells show a wide range in composition. A comparison of the analyses with pumpage data indicates that the groundwater samples with high barium concentrations represent periods when a greater component of groundwater was from the Ironton-Galesville.

Construction of municipal well Hanover Park-4 (fig. 13, 1a-1d) was completed in 1968. The well was drilled to a total depth of 437 meters (1434 ft) and the borehole was open to stratigraphic units from the Galena through the Ironton-Galesville. The bottom 12 meters (39 ft) of the borehole are in shale of the Eau Claire. Mechanical failure of the well due to the precipitation of secondary barite in the pump occurred in March 1975.

The highest barium concentrations occurred in groundwater samples collected during periods when the well was extensively pumped. The highest barium concentration in the available analyses is 7.0 mg/L for a sample collected in August 1976 (fig. 13, 1b). The lowest barite concentration, 0.8 mg/L, was for a sample collected in August 1980 during a period when the well was seldom used. (This analysis is not shown on figure 13.) The higher barium concentrations during periods of large groundwater withdrawals from the well are due to the production of a larger component of the groundwater from the Ironton-Galesville. A significant lateral variation also occurs in addition to the vertical variation in dissolved constituents in the Cambrian and Ordovician bedrock at the location of Hanover Park-4; the well is sited where a regionally significant change occurs in barium and sulfate concentrations in groundwater from the Ironton-Galesville. The effect of lateral mixing of groundwater from the Ironton-Galesville increases the supersaturation in the mixed groundwater in the well bore during periods of extensive pumpage.

Construction of municipal well Lake Zurich-5 (fig. 13, 4a-4d) was completed in 1963. The borehole of the well is open to stratigraphic

units from the Galena through the Ironton-Galesville. The well was drilled 9.8 meters (32 ft) into the Eau Claire, a total depth of 408.4 meters (1340 ft). Lake Zurich-5 is the first well on record to require maintenance because of secondary barite precipitation; failure of the well pump occurred in May 1972.

Analyses of seven groundwater samples collected from Lake Zurich-5 over the period 1963-1980 show barium concentrations ranging from 0.06 to 2.7 mg/L and sulfate concentrations ranging from 19.3 to 178 mg/L. The highest barium concentrations are in groundwater samples collected in 1971, 1972, and 1978 (fig. 13, 4a-4c) during periods of extensive pumpage. Except for a period of 1978, the well has not been used since 1975 as a source of groundwater supply to the community. The analyses with low barium and high sulfate concentrations are for groundwater samples collected in December 1980 (fig. 13, 4d) and August 1976, during periods when the well was not used as a community water supply. The great variation in barium and sulfate concentrations in the analyses indicates significant differences in the chemical composition of groundwater produced from different stratigraphic units open to the borehole. Native groundwater in the Ironton-Galesville has a high barium concentration and a low sulfate concentration. Groundwater with high sulfate concentrations and low barium concentrations is produced from less productive bedrock that has a higher hydraulic head than the Ironton-Galesville. Unfortunately, there is no information on the chemical composition of groundwater in the region of Lake Zurich in the St. Peter. The groundwater samples with low barium concentrations collected from this well in 1963, 1976, and 1980 may represent groundwater from the St. Peter.

Construction of the community well Lake Barrington Shores-2 (fig. 13, 3a-3c) was completed in 1976. The borehole of the well is open to stratigraphic units from the Galena through the Ironton-Galesville. The borehole extends 4.6 meters (15 ft) into the Eau Claire for a total depth of 398 meters (1305 ft). The well failed in March 1980 because of secondary precipitation of barite on the pump and the pump intake screen. Barium concentration in four groundwater samples collected from the well over the period 1976 to 1980 ranged

from 0.5 to 8.4 mg/L. The sulfate concentration in the four samples ranged from 10.6 to 314 mg/L.

The high sulfate concentration of 314 mg/L (fig. 13, 3b) was determined for a groundwater sample collected in May 1980 during a production test performed after the well was rehabilitated. Lake Barrington Shores groundwater is supplied not only from the deep well open to the Cambrian and Ordovician bedrock, but also from a shallow well finished in sand and gravel in the glacial drift with a total depth of 39.3 meters (129 ft). Both wells are connected to a common distribution system; check valves prevent the flow of groundwater from one well down the borehole of the other. The chemical composition of the groundwater sample collected from the deep well in May 1980 closely resembles that of groundwater produced by the shallow well. This analysis suggests that the check valve in the distribution system failed and that groundwater from the shallow well was pumped down the borehole of the deep well; mixing of the shallow groundwater containing high sulfate concentrations with groundwater containing high barium concentrations resulted in secondary precipitation of barite.

Analyses 3a and 3c (fig. 13) show that groundwater produced from the well in September 1978 and December 1980 was extremely supersaturated with regard to barite. A component of groundwater from the glacial drift cannot be recognized in these chemical analyses. The analyses indicate that there is potential for precipitation of secondary barite within the well because of the mixing of dissimilar groundwaters produced from the Cambrian and Ordovician bedrock.

Construction of municipal well Elgin-3A (fig. 13, 2a-2c) was completed in August 1967; this is one of five wells in a well field located on the west side of Elgin. The well was drilled to a depth of 420 meters (1378 ft) and the borehole is open to stratigraphic units from the Galena through the Ironton-Galesville. The bottom 16.1 meters (53 ft) of the borehole is in interlayered shale and dolomite of the Proviso Member of the Eau Claire Formation. A stratigraphic record of Elgin 3-A follows:

<u>Strata</u>	<u>Thickness</u>		<u>Depth</u>	
	(meters)	(feet)	(meters)	(feet)
Quaternary System				
Pleistocene Series				
glacial drift	48.2	158	48.2	158
Silurian System				
Alexandrian Series	3.7	12	51.8	170
Ordovician System				
Maquoketa Group				
shale, some dolomite	63.1	207	114.9	377
Galena Dolomite Group	80.2	263	195.1	640
Platteville Dolomite Group	17.7	58	212.8	698
Ansell Group				
Glenwood-St. Peter Sandstone	82.9	272	295.7	970
Cambrian System				
Eminence Formation and Potosi Dolomite	30.5	100	326.2	1070
Franconia Formation				
dolomite, shale, sandstone	21.3	70	347.5	1140
Ironton-Galesville Sandstone	56.4	185	403.9	1325
Eau Claire Formation				
Proviso Siltstone Member				
dolomite and shale	16.1	53	420.0	1378

The well has failed several times because of secondary barite precipitation. The first failure occurred in October, 1977, the most recent in January and November, 1982.

Analyses of four samples collected from 1972 to 1980 determined that the concentration of barium in groundwater pumped from Elgin-3A ranged from 3.5 to 10.9 mg/L. The sulfate concentration in the samples ranged from 10 to 13 mg/L. The degree of supersaturation in the 1972 samples (fig. 13, 2a) is much less than in samples collected in 1979 and 1980 (fig. 13, 2b and 2c).

Downhole geophysical measurements (temperature, conductance, and natural gamma radiation) were made in the open borehole as part of the present research. Downhole groundwater samples were also collected. During these tests, the bottom of the open borehole was measured at 403 meters (1322 ft); the lower 16.8 meters (55 ft) of the well had filled in with rock debris from the wall of the borehole. The 403-meter (1322-ft) depth is 0.9 meters (3 ft) above the contact of the Galesville Sandstone with the Eau Claire Formation. The measurements of temperature

and conductance of groundwater in the open borehole determined that groundwater from the upper aquifer units was flowing down the open borehole and into the Ironton-Galesville.

The record of the downhole natural gamma radiation measurements determined the extensive presence of anomalously high natural gamma radiation in the borehole. The high radiation values are interpreted as due to the coprecipitation of radium with barium during the secondary precipitation of barite on the rock matrix in the wall of the open borehole. ^{226}Ra and ^{228}Ra were present in a sample of barium sulfate precipitate collected from the pump intake check valve. The anomalously high natural gamma radiation was present in the depth interval from 266.7 meters (875 ft) to the bottom of the borehole. Extremely high natural gamma radiation was measured in the open borehole over the interval from 315 meters (1034 ft) to the bottom of the open borehole. High natural gamma radiation was also measured in the depth interval of 213 meters (700 ft) to 218 meters (715 ft) and 227 meters (745 ft) to 235 meters (770 ft). These zones reflect precipitation of secondary barite at two different setting depths for the well pump intake.

In 1982 chemical analyses were performed on groundwater samples collected with a downhole sampler at five discrete depths in the open borehole. A filtered sample (0.45 micron membrane) collected at 198 meters (650 ft) where the borehole is open to the Galena and Platteville had a dissolved barium concentration of 0.71 mg/L and a dissolved sulfate concentration of 30 mg/L.

The downhole sample collected at a depth of 259 meters (850 ft) where the borehole is open to the St. Peter Sandstone is a mixture of groundwater from the Galena and Platteville and the St. Peter. A sample filtered at the well site (0.45 micron pore size membrane) contained a dissolved barium concentration of 19.0 mg/L and a dissolved sulfate concentration of 12 mg/L. Note the significant difference in barium concentration between the 198-meter (650-ft) and the 259-meter (850-ft) samples.

The downhole groundwater sample collected at a depth of 320 meters (1050 ft) where the borehole is open to the Eminence and Potosi

is a mixture of groundwater produced from the Galena and Platteville, the Glenwood-St. Peter, the Eminence and Potosi. At the time of collection, fine particles of secondary barite were observed to be suspended in the sample. An analysis of an unfiltered sample determined that the barium concentration was 20.4 mg/L and the sulfate concentration was 28.3 mg/L.

The downhole groundwater sample collected at a depth of 390 meters (1280 ft) where the borehole is open to the Galesville Sandstone is a mixture of groundwater produced from the Galena and Platteville through the upper section of the Eau Claire. Analysis determined a dissolved barium concentration of 17.0 mg/L and a dissolved sulfate concentration of 22.0 mg/L for a sample filtered at the well site (0.45 micron membrane).

The deepest downhole sample was collected at the bottom of the open borehole at a depth of 403 meters (1322 ft). At this depth, a sandpump was used to collect groundwater and sediments from the bottom of the well. The sediments were a heterogeneous mixture of materials that sloughed off the wall of the borehole. Analyses of a sample filtered at the well site (0.45 micron membrane) determined a barium concentration of 8.3 mg/L, a sulfate concentration of 12 mg/L, and a chloride concentration of 80 mg/L. The concentrations of barium and sulfate in the sample are lower than the concentrations in the sample collected at 390 meters. The lower concentrations are thought to be due to the longer residence time of the groundwater in the sloughed material. The high chloride concentration is interpreted to indicate that a portion of this groundwater sample was from the Proviso Siltstone Member of the Eau Claire. The available chemical analyses indicate that a significant increase in the chloride concentration in groundwater pumped from Elgin-3A occurred between the years 1972 and 1976. Between 1972 and 1976, the chloride concentration increased from 7 to 40 mg/L; an analysis in 1980 determined a concentration of 59 mg/L. The concentration of chloride is significantly higher in this well than in other wells in the well field.

Elgin-3A is the only well of five in the well field that is experiencing pump failure due to precipitation of secondary barite. The pump failures began after the increase in the chloride concentration

in groundwater pumped from the well. The increase in chloride concentration in groundwater pumped from the well is interpreted as due to the initiation of production of a significant component of groundwater from the Proviso. The production of groundwater from the Proviso is believed to result from a marked decrease in hydraulic head in the Iron-ton-Galesville due to the large withdrawals of groundwater from the well field. The concentration of sulfate in groundwater produced from the Proviso created extreme disequilibrium with regard to barite solubility in the mixed groundwater and resulted in massive barite precipitation in the well pump. The cross-formational flow of groundwater from the Proviso to the Iron-ton-Galesville may not be restricted to the open borehole. When the well was constructed in 1967, explosives were used to increase the production of groundwater from the Iron-ton-Galesville Sandstone. It is possible that the use of explosives caused fractures in the upper bedrock in the Proviso Member. The fractures could be pathways for the flow of groundwater.

Municipal well Elgin-3A is a large-capacity well with a sustained yield greater than 4160 liters per minute (1100 gallons per minute). It is located in a well field that is a vital source of water to the community of Elgin. The other four municipal wells in this field have not experienced maintenance problems due to barite precipitation. The other wells are constructed similarly to Elgin-3A; they produce groundwater with high concentrations of dissolved barium. However, the high chloride concentrations are present only in groundwater from well 3A. The chloride concentration in the other wells in the well field on the west side of Elgin should be monitored closely. At the present time, groundwater produced from these wells is greatly supersaturated with respect to barite. Analyses numbers 7 and 8 in figure 13 illustrate the high degree of supersaturation present in groundwater produced from two of the wells. The entry of groundwater from the Proviso Siltstone Member of the Eau Claire Formation into these wells may lead to the secondary precipitation of barite. An increase in chloride concentration would be a signal that the Proviso was contributing groundwater to the wells.

Three remedial measures may be effective in controlling the secondary barite precipitation at municipal well Elgin-3A. It is possible that application of any of the three measures may eliminate the problem of well failure due to barite precipitation.

1. Constructing the well with cemented casing to a depth of 232 meters (760 ft) will prevent entry of groundwater with a high concentration of sulfate from the Galena and Platteville. The installation of cemented casing to the 232 meter (760 ft) depth will also prevent entry of groundwater from the Glenwood Formation, a highly varied unit of sandstone, dolomite, and shale overlying the St. Peter Sandstone. The chemical composition of groundwater in the Glenwood is not known. However, there is a possibility that the groundwater from this bedrock unit may have a high sulfate concentration.

2. The installation of 30.5 meter (100 ft) of cemented casing in the depth interval of 293.7 meters (970 ft) to 326.2 meters (1070 ft) will prevent the production of groundwater with a high sulfate concentration from the Eminence and Potosi.

3. Deepening the borehole to produce groundwater from the Elmhurst Sandstone Member of the Eau Claire Formation and the upper section of the Mt. Simon Sandstone will reduce the production of groundwater with high concentrations of chloride and sulfate from the Proviso of the Eau Claire. An additional advantage of this measure is that long-term productivity of the well (and the well field) will be increased. Lowered pumping costs may also result from a higher pumping water level in the well. It is important not to drill deep into the Mt. Simon where groundwater is very mineralized with high chloride and sulfate concentrations. Construction of the well to a total depth of greater than 580 meters (1902 ft) is not recommended.

The downhole methods (geophysical and groundwater sampling) used at Elgin can be used in determining remedial measures to prevent secondary barite precipitation in the wells Hanover Park-4, Lake Zurich-5, and Lake Barrington Shores-2. Analyses of groundwater samples collected from discrete stratigraphic units would permit identification of the bedrock that produces groundwater with high sulfate concentrations. The emplacement of cemented casing from the land surface downward through the

St. Peter may be necessary to prevent high maintenance costs at these wells due to secondary barite precipitation; however, the barium concentrations in groundwater produced from the wells will be high, and the yield of groundwater from the wells may be reduced.

An alternative measure for the Lake Barrington Shores well would be to backfill the borehole and seal off production of groundwater from the Ironton-Galesville. This measure would lower the concentration of barium in groundwater, perhaps to a concentration within compliance of the drinking water regulations. Sealing off the Ironton-Galesville will greatly reduce the yield of the well. However, the St. Peter may be capable of producing a sufficient supply of groundwater for the community.

BARIUM IN GROUNDWATER AT LOCATIONS OUTSIDE NORTHEASTERN ILLINOIS

An inventory of chemical analyses on public groundwater supplies in Illinois (outside the region of northeastern Illinois shown in figure 11) determined that the barium concentrations in untreated groundwater were generally insignificant. However, at many restricted locations throughout Illinois, analyses of groundwater from public and domestic wells determined barium concentrations greater than 1.0 mg/L. The analytical data available on barium in groundwater of Illinois primarily relates to public water supplies; analysis for barium is rarely performed on groundwater samples collected from domestic or industrial supplies. Because of the limited data base, it is not possible to evaluate accurately the occurrence of barium at significant concentrations in aquifer strata that provide domestic supplies of groundwater but do not produce sufficient groundwater for public supplies.

The data base on sulfate concentration in groundwater from domestic wells is much larger than the data base on barium concentration in groundwater from domestic wells. The sulfate concentration may be used to evaluate the presence of a significant barium concentration. Groundwater that contains a sulfate concentration of 10 mg/L or greater will generally have a barium concentration much less than 1.0 mg/L. A groundwater analysis that could indicate the possibility of a barium concentration of 1.0 mg/L or greater would be a sulfate concentration

of less than 10 mg/L, the presence of hydrogen sulfide, and an alkalinity greater than the hardness when both are expressed as equivalents of calcium carbonate. These characteristics indicate an anaerobic environment in which sulfate concentrations may be low because of microbially mediated reactions. Barium may occur in the sulfate-depleted groundwater at high concentrations. However, the presence of barium in groundwater requires a source of barium in the aquifer matrix. Quite often groundwater with a very low sulfate concentration also has a low barium concentration because there is no significant source of barium from the matrix.

Analyses of groundwater from public and domestic wells in north-central and northwestern Illinois that produce groundwater from stratigraphic units of the Ordovician System have identified a region of southern Stephenson County, northwestern Ogle County and northern Carroll County where groundwater from wells finished in the Cambrian and Ordovician bedrock may have barium concentrations greater than the drinking water regulation of 1.0 mg/L. Groundwater with the highest barium concentration (21.0 mg/L) was from a domestic well in Stephenson County that has the borehole open to the Glenwood-St. Peter Sandstone. A barium concentration of 3.0 mg/L was determined for a groundwater sample from municipal well no. 2 at Shannon in Carroll County that has an open borehole in the interval Galena through St. Peter. Analysis of a groundwater sample from municipal well no. 1 at German Valley in Stephenson County determined a barium concentration of 4.9 mg/L. The borehole of this well is open only to the St. Peter. In the vicinity of German Valley, the Maquoketa is absent and the anaerobic environment in the St. Peter is due to confinement by the Galena and Platteville. Municipal well no. 2 at German Valley is near municipal well no. 1, but is constructed with the borehole open only to the Galena and Platteville. Analysis of a groundwater sample collected from this well determined a barium concentration of 0.3 mg/L. Analysis of groundwater samples from two domestic wells in the vicinity of German Valley that are constructed with boreholes open only to the Galena and Platteville determined low barium concentrations of 0.1 mg/L.

An inventory of the available data has determined the widespread occurrence of groundwater in Illinois with a significant barium concentration from aquifers other than rocks of the Cambrian and Ordovician Systems. Aquifer strata include glacial drift, fractured shale and sandstone of the Pennsylvanian System, and dolomite of the Devonian and Silurian Systems. Barium concentrations in untreated groundwater samples range from 0.4 mg/L to 3.9 mg/L.

Within Illinois there is a large, widely distributed set of chemical analyses on public supplies of groundwater from sand and gravel in the glacial drift. The analyses indicate that although there is a great range in sulfate concentrations in groundwater from the glacial drift, the barium concentrations are generally very low. Often the sulfate concentrations are low and the analyses indicate that an anaerobic environment is present. However, barium concentrations in groundwater from these wells are also very low, with one known exception. The low barium concentrations probably reflect the absence of a source for barium in the aquifer matrix.

The exception is a community well located at Farmer City in De Witt County. The sand and gravel deposit that produces groundwater to the well is overlain and confined by a thick sequence of fine-grained glacial tills. The sand and gravel is located at the base of the glacial materials and overlies shale bedrock of the Pennsylvanian System. The groundwater from these deposits is anaerobic and contains methane gas. The Eh measured with platinum electrodes was -165 millivolts. The concentration of barium in three groundwater samples collected from the well range from 0.7 to 1.2 mg/L. The shale bedrock may be the source for the barium present in the groundwater.

SUMMARY

NATURAL RADIOISOTOPES IN GROUNDWATER

The concentrations of ^{222}Rn , ^{226}Ra , ^{228}Ra , ^{234}U and ^{238}U in groundwater were investigated as part of a study of mechanisms responsible for high concentrations of ^{226}Ra and ^{228}Ra in groundwater from the Cambrian and Ordovician bedrock in northern Illinois. A limited number of analyses were performed for ^{232}Th and ^{230}Th in groundwater.

The concentration of dissolved ^{226}Ra in potable groundwater ranged from 0.2 to 36.9 pCi/L. A concentration of 40.2 pCi/L was measured in a brine sample from the Mt. Simon Sandstone. The lowest concentrations are present in primary recharge zones in north-central Illinois where groundwater has a short residence time in the Cambrian and Ordovician bedrock. Along flow paths away from the zone of recharge there is an increase in dissolved ^{226}Ra concentrations. The highest concentrations occur in mineralized groundwater in locations where the Cambrian and Ordovician bedrock is confined. An important mechanism related to the concentration of ^{226}Ra in groundwater is the transport of ^{238}U and ^{234}U in groundwater, and subsequent secondary accumulation of ^{238}U , ^{234}U , and ^{230}Th on the matrix of the sandstone bedrock. The ionic strength of groundwater is an important control on the desorption of ^{226}Ra from the matrix. In some localities the dissolved ^{226}Ra concentrations are affected by precipitation-dissolution of secondary barite.

The concentration of dissolved ^{228}Ra in potable groundwater from the Cambrian and Ordovician bedrock ranged from 0.4 to 18.9 pCi/L. A concentration of 32.7 pCi/L was measured in mineralized groundwater from the Mt. Simon Sandstone. Over a large part of northern Illinois the dissolved ^{228}Ra concentrations are less than 3.0 pCi/L. The high concentrations of ^{228}Ra are present in localities of northeastern Illinois. Unlike the concentration of ^{226}Ra , the concentration of dissolved ^{228}Ra is not directly related to the ionic strength of groundwater. In some localities the ^{228}Ra concentrations are affected by precipitation-dissolution of secondary barite. A primary control on the

concentration of ^{228}Ra in groundwater may be the abundance of accessory minerals in the bedrock that contain the ^{232}Th parent.

The combined concentration of ^{226}Ra and ^{228}Ra in groundwater of the Cambrian and Ordovician bedrock ranged from 2.3 to 50.2 pCi/L. Most analyses exceed the 5.0 pCi/L maximum contaminant level for the combined concentration of the two nuclides. The $^{226}\text{Ra}/^{228}\text{Ra}$ activity ratio ranged from 0.2 to 41.0. The concentrations of the two nuclides in groundwater are not related and a ^{226}Ra analysis has no validity for prediction of the ^{228}Ra concentration.

The comparison of historical and recent analyses determined that the concentration of ^{226}Ra and ^{228}Ra produced from most public supply wells has not changed over time. The gross alpha radiation analyses performed on public supply wells over a 6-year period created a specter that the groundwater was increasing in radioactivity; the variation in the gross alpha concentration (with a general trend of increase) was actually due to an uncontrolled variable in the analytical method.

Analyses determined that the high dissolved concentrations of ^{226}Ra and ^{228}Ra are present in groundwater from sandstones—the productive aquifers in the Cambrian and Ordovician bedrock. Therefore, remedial well construction measures will not lower the concentrations. In north-eastern Illinois the highest dissolved concentrations in potable groundwater are from the Ironton-Galesville Sandstone. Therefore, radium concentrations may increase in the future in groundwater from wells in localities where the aquifers above the Ironton-Galesville are being dewatered by large withdrawals.

The mass concentration of uranium in groundwater from the Cambrian and Ordovician bedrock ranged from <0.002 to 1.10 $\mu\text{g/L}$. The lowest concentrations were present in groundwater with a low Eh. The combined activity concentrations of ^{234}U and ^{238}U ranged from <0.1 to 7.9 pCi/L and were less than the 10.0 pCi/L maximum contaminant level determined for drinking water in a very preliminary study. The $^{234}\text{U}/^{238}\text{U}$ activity ratios for groundwater from the Cambrian and Ordovician bedrock ranged from 2.1 to 40.7. The lowest activity ratios were present in groundwater in primary recharge zones. Downgradient, in the direction of flow, the activity ratios increase and values greater than 20 occur

widely in northern Illinois. The extreme enrichment in ^{234}U in groundwater was unexpected and the mechanisms responsible are not well understood. The high activity ratios are thought to reflect a diffuse secondary accumulation of uranium on the sandstone matrix. The presence of the uranium may be significantly related to recharge events related to glacial processes.

The concentration of ^{222}Rn in groundwater from the Cambrian and Ordovician bedrock ranged from 40 to 670 pCi/L. The concentrations are much less than the proposed maximum contaminant level of 10,000 pCi/L for drinking water. ^{222}Rn is an inert gas with a short half-life that is generated by the disintegration of ^{226}Ra . However, the dissolved concentrations of ^{222}Rn and ^{226}Ra are not directly related. Some of the highest ^{222}Rn concentrations are in groundwater with the lowest concentrations of ^{226}Ra . For all analyses the ^{222}Rn concentrations were at least an order of magnitude greater than the ^{226}Ra concentrations. The ^{222}Rn concentrations indicate that ^{226}Ra is ubiquitous on the aquifer matrix and that geochemical mechanisms control the concentration of ^{226}Ra in solution.

Thorium ions have ultratrace solubilities in aqueous systems. In the present research, seven groundwater samples were analyzed for ^{232}Th and ^{230}Th . The isotopes were not detected in any of the analyses. The limit of detection for the analytical method is 0.01 $\mu\text{g/L}$ expressed as ^{232}Th .

BARIUM IN GROUNDWATER

High dissolved barium concentrations in the Cambrian and Ordovician bedrock of northern Illinois occur in groundwater anomalously depleted in dissolved sulfate. The depletion of dissolved sulfate is due to bacterially mediated reactions in anaerobic environments of the bedrock. In northeastern Illinois the anaerobic environments exist in aquifer units overlain and confined by the Maquoketa Shale Group. In some localities of north-central and northwestern Illinois where the Maquoketa is absent, anaerobic environments are present where dense, unfractured dolomites of the Galena and Platteville Groups overlie the aquifer units.

The most extensive area in which high dissolved barium concentrations occur in the Cambrian and Ordovician bedrock is in northeastern Illinois. Within this area, barium concentrations greater than 5 mg/L are widespread, and concentrations greater than 20 mg/L are measured in groundwater at a few wells. Significantly, the high dissolved barium concentrations are present in the stratigraphic units that are the most productive aquifers—the St. Peter Sandstone and the Ironton-Galesville Sandstone. The available analyses indicate that in northeastern Illinois the highest dissolved barium concentrations occur in the most productive aquifer, the Ironton-Galesville Sandstone. Therefore, remedial well construction measures will not lower barium concentrations in groundwater from high-capacity wells.

After depletion of sulfates within the aquifer units, the dissolved barium concentrations are not controlled by the solubility of barite and may be present at high concentrations. Feldspars present as accessory minerals in the sandstone matrix are a possible source of barium.

Maps were constructed showing the distribution of dissolved barium and sulfate in groundwater from the Cambrian and Ordovician bedrock in northeastern Illinois. Regional planners or municipal water superintendents involved in decisions concerning the location of new wells drilled into the Cambrian and Ordovician bedrock should find these maps helpful.

Several wells in northeastern Illinois produce groundwater that is extremely supersaturated with respect to barite. Four wells have required expensive maintenance because of the massive precipitation of barite in the well pump and discharge pipe. A remedial measure that may prevent the barite precipitation is to construct these wells with cemented casing to prevent entry of groundwater from the less productive bedrock units that produce groundwater having high dissolved sulfate concentrations.

At many locations in Illinois, barium concentrations greater than 1.0 mg/L are present in anaerobic groundwater from aquifers other than bedrock of the Cambrian and Ordovician Systems. Aquifer strata

include fractured shale and sandstone of the Pennsylvanian System and dolomite of the Devonian and Silurian System. Because of the limited data, it is not possible to evaluate accurately the regional occurrence of dissolved barium in groundwater from these aquifers that provide important domestic supplies of groundwater but do not produce the quantity of groundwater necessary for public supplies.

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